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(54) Title: POLYMERS, THEIR PRECURSORS AND PROCESSES FOR PREPARATION THEREOF

(57) Abstract: Novel block polymers of ethylenically unsaturated monomers and ethylenically unsaturated carboxylates such as vinyl acetate may be made by transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate, such as vinyl acetate. Also, novel α, ω di-functional polymer precursors may be made by the steps of (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

**POLYMERS, THEIR PRECURSORS AND PROCESSES FOR PREPARATION
THEREOF**

The present invention relates to a process for preparing polymers, novel polymers, a process for preparing polymer precursors and novel polymer precursors.

The preparation of polymers by transition metal mediated, atom transfer polymerisation processes is known, see for example K. Matyjaszewski in '*Controlled*
5 *Radical Polymerisation*', American Chemical Society, 1998. Transition metal mediated, atom transfer polymerisation processes involve the polymerisation of a monomer in the presence of (i) a transition metal in a low valency state, usually present as the halide, preferably chloride or bromide, (ii) an organodiimine and (iii) an initiator compound comprising a homolytically cleavable bond with a halogen atom.

10 Wang J-S et al in *Macromolecules* 1995, 28, 7901-7910 describe an atom transfer polymerisation process using an alkyl halide R-X (X= Cl and Br) and a transition metal species complexed by suitable ligand(s) M_t^n/L_x such as $CuX/2,2'$ -bipyridine for the polymerisation of styrenes and (meth)acrylates.

15 International Patent Publication WO97/47661 describes a process for the atom transfer polymerisation of olefinically unsaturated monomers in the presence of (i) a transition metal such as copper, (ii) an organodiimine wherein at least one of the nitrogens of the diimine is not part of an aromatic ring such as a 1,4-diaza-1,3-butadiene, a pyridinecarbaldehyde, an oxazolidone or a quinoline carbaldehyde and (iii) an initiator compound comprising a homolytically breakable bond with a halogen atom.

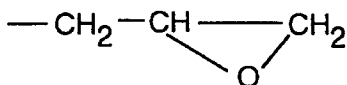
20 It has now been found that block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as

styrene, acrylates and methacrylates can be prepared by transition metal mediated, atom transfer polymerisation.

According to a first aspect of the present invention there is provided a process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate. A preferred ethylenically unsaturated carboxylate is vinyl acetate. Such block polymers are believed to be of the ABA type.

According to this aspect of the present invention, the transition metal mediated, atom transfer polymerisation may be preformed in the presence of (i) a first component represented by MY where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion, (ii) an organodiimine, (iii) the α, ω di-functional polymer precursor and (iv) an ethylenically unsaturated monomer.

The ethylenically unsaturated monomer may be : styrene; acrylonitrile; methacrylonitrile; acrylamide; methacrylamide; acrylic acid; unsubstituted acrylate for example having a formula $H_2C=CH-CO_2Z$ in which Z is methyl, allyl, or a functional group such as $-CH_2CH_2OH$ or $-CH_2CH_2N(CH_3)_2$; or a methacrylate for example having a formula $H_2C=C(CH_3)-CO_2Z'$ in which Z' is H, methyl, allyl, benzyl, or a functional group such as $-CH_2CH_2OH$, $-CH_2CH_2N(CH_3)_2$, $-CH_2-CH=CH_2$, $-CH_2NH_3^+Cl^-$ or



In the first component represented by MY, M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion. Suitable transition metals, M may be Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), preferably, Cu(I). The non-charged ligand may be CH_3CN . Y may be chosen from Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3).

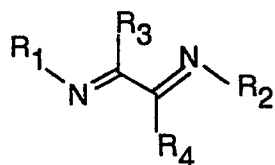
Suitably, the transition metal component and the organodiimine are present as a complex represented by the formula $[ML_m]^{n+} A^{n-}$ wherein M is a transition metal in a low

valency state; L is an organodiimine; A^{n-} is an anion; n is an integer of 1 to 3; and m is an integer of 1 to 2. Suitable transition metals M, may be Cu(I), Fe(II), Co(II), Ru(II) and Ni(II), preferably, Cu(I). Suitably, A represents Cl, Br, F, I, NO_3 , PF_6 , BF_4 , SO_4 , CN, SPh, SCN, SePh or triflate (CF_3SO_3). Most preferably, as $[ML_m]^{n+} A^{n-}$ there is used

5 CuBr.

The organodiimine may be :

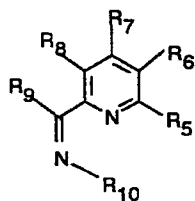
a 1,4-diaza-1,3-butadiene such as represented by Formula (1) :



10

Formula (1)

a 2-pyridinecarbaldehyde imine such as represented by the Formula (2) :

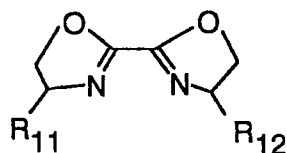


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Formula (2)

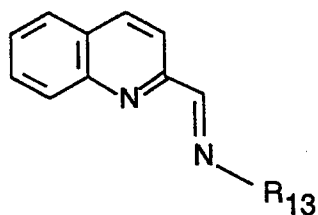
an oxazolidone such as represented by Formula (3) :

20



Formula (3)

or a quinoline carbaldehyde such as represented by Formula (4) :



5

Formula (4)

- wherein R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be varied independently and R_1 , R_2 , R_{10} , R_{11} , R_{12} and R_{13} may be H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or substituted phenyl where substitution is as described for R_4 to R_9), CH_2Ar (where Ar = aryl or substituted aryl) or a halogen. Preferably, R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may be a C_1 to C_{20} alkyl, hydroxyalkyl or carboxyalkyl in particular C_1 to C_4 alkyl, especially methyl or ethyl, n-propyl, isopropyl, n-butyl, *sec*-butyl, *tert*. butyl, cyclohexyl, 2-ethylhexyl, octyl, decyl or lauryl. R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} may especially be methyl.

R_3 to R_9 may independently be selected from the group described for R_1 , R_2 , R_{10} , R_{11} , R_{12} , and R_{13} and OCH_{2n+1} (where n is an integer from 1 to 20), NO_2 , CN, and $O=CR$ (where R = alkyl, benzyl, $PHCH_2$ or a substituted benzyl, preferably a C_1 to C_{20} alkyl, especially a C_1 to C_4 alkyl).

The organodiimine may exhibit a chiral centre α to one of the nitrogen groups.

Compounds of Formula (2) may comprise one or more fused rings on the pyridine group.

One or more adjacent R_1 and R_3 , R_3 and R_4 , R_4 and R_2 , R_{10} and R_9 , R_8 and R_9 , R_3 and R_7 , R_7 and R_6 , R_6 and R_5 groups may be C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norbornenyl.

Preferred organodiimines include compounds represented by Formula (2) in which $R_5 = R_6 = R_7 = R_8 = R_9 = H$ and R_{10} is selected from the group consisting of : C_2H_5 -, $n-C_3H_7$ -, $(CH_3)_2CH$ -, $cycloC_3H_5$ -, $n-C_5H_{11}$ -, $n-C_6H_{13}$ -, $n-C_7H_{15}$ -, $n-C_8H_{17}$ -, $n-C_9H_{19}$ -, $n-C_{18}H_{37}$ -, $CH_3(C_2H_5)CH-CH_2$ -, $HO-CH_2-CH_2$ -, $HO-CH_2-CH_2-CH_2$ -,

HC*(CH₃)Ph (R form), HC*(CH₃)Ph (S form), HC*(CH₃)Ph (RS form), HO₂CCH₂- and HO₂CC*H(R₁₄)- wherein * indicates a chiral centre, Ph is a phenyl group and R₁₄ is hydrogen, C₁ to C₁₀ branched alkyl, carboxy- or hydroxy- C₁ to C₁₀ alkyl. Preferred organodiimines represented by Formula (2) include n-propyl-pyridinal methanimine and
 5 n-octyl-pyridinal methanimine.

Other suitable catalyst systems for the atom transfer polymerisation included :

- (I) RuCl₂(PPh₃)₃/CCl₄/methylaluminium bis-(2,6-di-*tert*-butylphenoxide); NiBr₂(PPh₃)₂, NiBr₂(PnBu₃)₂; and FeCl₂(PPh₃)₂ being described in *Macromolecules* 1995, 28, 1721; *Macromolecules* 1997, 30, 2249; and
 10 *Macromolecules* 1997, 30, 4507, the contents of which are hereby incorporated by reference;
- (II) Cu(I)Br/ligand/initiator/monomer/solvent in which the initiator is RX, methyl 2-bromopropionate, ethyl 2-bromopropionate, 1-phenylethyl bromide or ethyl 2-bromoisobutyrate and the ligand is a derivative of 2,2'-bipyridine or simple
 15 aliphatic polyamines, being described in *Macromolecules* 1999, 32, 290 and 1767; *Macromolecules* 1997, 30, 7967; *Macromolecules* 1995, 28, 7901; and J. Am. Chem. Soc. 1995, 117, 5614 the contents are hereby incorporated by reference.
- (III) [Ni{o,o'-(CH₂-NMe₂)₂C₆H₃}Br] with an initiator of CCl₄, 2-bromoisobutylphenone or 2-bromoethylisobutrate, being described in
 20 *Macromolecules* 1996, 29, 8576, the contents of which are hereby incorporated by reference.
- (IV) RhCl(PPh₃)₃ with dichloroacetophenone and 7 equivalents of triphenylphosphine, being described in *Macromolecules* 1998, 31, 542, the contents of which are
 25 hereby incorporated by reference.
- (V) [Pd(OAc)₂] with carbon tetrachloride and triphenylphosphine, being described in *Macromolecules* 1997, 30, 7631, the contents of which are hereby incorporated by reference.
- (VI) Cu(I)Cl/2,2'-bipyridine with arenesulfonyl chlorides being described in
 30 *Macromolecules* 1995, 28, 7970, the contents of which are hereby incorporated by reference.

The transition metal, mediated atom transfer polymerisation process may be preformed using conditions known in the art, for example such as described in International patent publication WO 97/47661, the contents of which are hereby incorporated by reference.

5 The atom transfer polymerisation process may be performed either using a solvent or in bulk, preferably in bulk due to the formation of gels. Non protic solvents may be used. Suitable solvents include hydrocarbons, anisole, ethyl acetate, diphenyl ether, higher alcohols, water and ketones such as acetone. Preferred solvents are xylene and toluene.

10 The atom transfer polymerisation process generally requires elevated temperature and this depends upon the catalyst system and monomers used. In particular, the polymerisation may be performed at a temperature in the range of -40°C to $+180^{\circ}\text{C}$, preferably 0°C to 150°C , more preferably in the range 10° to 130°C . Suitably 90°C may be used, although 110°C may be used for styrene co-polymerisation.

15 The polymerisation process is suitably performed at atmospheric pressure, although a higher pressure might be used.

In the polymerisation process, the molar ratio of ethylenically unsaturated monomer : α , ω di-functional polymer precursor initiator is suitably (3 to 100000) : 1, preferably (10 to 1000) : 1 more preferably (10 to 500) : 1.

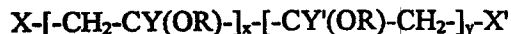
20 In the polymerisation process, the molar ratio of organodiimine ligand : transition metal is suitably (100 to 0.1) : 1, preferably (3 to 1) : 1.

In the polymerisation process, the molar ratio of α , ω di-functional polymer precursor initiator : transition metal is suitably (1000 to 0.01) : 1, preferably (10 to 0.5) : 1.

25 In the polymerisation process the concentration of monomer is suitably in the range 1 to 100 %, preferably in the range 20 to 50 %.

The α , ω di-functional polymer precursor acts as an initiator for the transition metal, atom transfer polymerisation process.

30 The α , ω di-functional polymer precursor may be a polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



wherein x and y are integers independently greater than 1; Y and Y' are independently H or -CH₃; R represents a hydrocarbonyl group; and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

R may be selected from the group consisting of: CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-, CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_zC(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F. Preferably, R is CH₃C(O)-.

The X and X' groups preferably have homolytically cleavable Cl and/or Br bonds. Preferably, X and X' are independently selected from the group consisting of:

BrCH₂C(O)O-; BrC(Me)₂C(O)O-;
BrCH₂C(O)OCH₂CH₂NHC(O)CMe₂-; and
BrCMe₂C(O)OCH₂CH₂NHC(O)CMe₂-.

wherein Me represents CH₃-.

Such novel polymer precursors may be prepared by the steps (a) and (b) of the process hereinafter described and may be used in a transition metal mediated, atom transfer polymerisation for the preparation of block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as styrene, (meth)acrylates, (meth)acrylonitriles and (meth)acrylamides.

Thus, according to another aspect of the present invention there is provided a process for the production of an α, ω di-functional polymer precursor which process comprises the steps of:

- (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and
- (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.

Preferably, the ethylenically unsaturated carboxylate is vinyl acetate optionally with other co-monomers known in the art.

Preferably, the radical initiator has a functional group selected from hydroxyl, carboxylic acid and amides, preferably hydroxyl. Suitably, the radical initiator having a hydroxyl function group is selected from hydrogen peroxide, azobis compounds having
5 hydroxyl or amide functional groups and benzoyl peroxide. Suitable azobis compounds are:

4,4'-azobis (4-cyanopentanoic acid),
2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]-propionamide},
10 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-ethyl]-propionamide} , and
2,2 - azobis(isobutyramide) dihydrate.

The reaction between the ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group in step (a) may be performed using conventional free radical polymerisation conditions, known in the art.

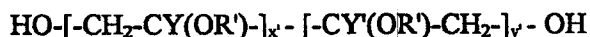
15 In step (b) the functional groups on the product of step (a) are substituted with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process. Preferably, such substituents have chlorine or bromine substituents α to an electron withdrawing activating group. Preferably, the electron withdrawing group of the substituent active for the formation of block polymers
20 in a transition metal mediated, atom transfer polymerisation process is selected from nitrile, ester and phenyl.

Preferably, in step (b) the product from step (a) is reacted with $\text{BrC}(\text{CH}_3)_2\text{C}(\text{O})\text{Br}$.

In step (b) the functional groups on the product of step (a) may be substituted
25 with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process under conventional conditions known in the art. Thus a reaction temperature of 0°C or room temperature may be used, depending upon the exotherm. Atmospheric pressure may suitably be used. Dry solvents are used, for example THF, pyridine and toluene. The brominating agent is
30 added in excess. Hydrogen bromide formed in the reaction may be removed, for example by precipitation as $\text{HBr} \cdot \text{NEt}_3$ with triethylamine.

The novel α, ω di-functional polymer precursors prepared according to this aspect of the present invention may be used in a transition metal mediated, atom transfer polymerisation for the preparation of block co-polymers of ethylenically unsaturated carboxylates such as vinyl acetate, with ethylenically unsaturated monomers such as styrene, (meth)acrylates, (meth)acrylonitriles and (meth)acrylamides.

According to a further aspect of the present invention there is provided a polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



wherein x' and y' are integers independently greater than 1; Y and Y' are independently H or -CH_3 ; and R' represents a hydrocarbyl group.

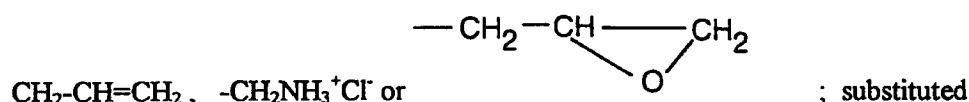
R' may be selected from the group consisting of: $\text{CH}_3\text{C(O)-}$, $\text{Y}''\text{-C(O)-}$, PhC(O)- , Ph-, $\text{PhCH}_2\text{-}$, $\text{CH}_3\text{-(CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{)-}_z\text{C(O)-}$, $\text{CH}_3\text{-(CH}_2\text{-CH=CH-CH}_2\text{)-}_z\text{C(O)-}$ and substituted phenyl; wherein Y'' is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO_2 , OMe, CN, NMe_2 , OH, CL, Br, and F. Preferably, R' is $\text{CH}_3\text{C(O)-}$.

Such novel polymer precursors may be prepared by step (a) and used in step (b) of the process hereinbefore described.

According to yet a further aspect of the present invention there is provided a block polymer comprising alternating repeating units of -[A]- and -[B]- in which : -A- represents a polymer block having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



wherein x'' and y'' are integers independently greater than 1; Y and Y' are independently H or -CH_3 and R'' represents a hydrocarbyl group; and -B- represents at least one polymer repeating unit selected from the group consisting of acrylic; substituted acrylic for example, having a formula $\text{-HC-C-(CO}_2\text{Z)-}$ in which Z in which Z is methyl, allyl, or a functional group such as $\text{-CH}_2\text{CH}_2\text{OH}$ or $\text{-CH}_2\text{CH}_2\text{N(CH}_3\text{)}_2$; methacrylic for example, having a formula $\text{-HC-C(CH}_3\text{)-(CO}_2\text{Z')-}$ in which Z' is H, methyl, allyl, benzyl, or a functional group such as $\text{-CH}_2\text{CH}_2\text{OH}$, $\text{-CH}_2\text{CH}_2\text{N(CH}_3\text{)}_2$, -



$\text{CH}_2\text{---CH=CH}_2$, $\text{---CH}_2\text{NH}_3^+\text{Cl}^-$ or

; substituted

methacrylic; acrylonitrile; methacrylonitrile; acylamide; methacrylamide and styrenic polymer repeating units and is preferably at least one methacrylic, styrenic and/or n-butyl methacrylic repeating unit.

- 5 R'' may be selected from the group consisting of: $\text{CH}_3\text{C(O)---}$, $\text{Y}''\text{---C(O)---}$, PhC(O)--- , Ph--- , $\text{PhCH}_2\text{---}$, $\text{CH}_3\text{---(CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---)}_x\text{C(O)---}$, $\text{CH}_3\text{---(CH}_2\text{---CH=CH---CH}_2\text{---)}_x\text{C(O)---}$ and substituted phenyl; wherein Y'' is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent
- 10 selected from the group consisting of NO_2 , OMe, CN, NMe_2 , OH, Cl, Br, and F. Preferably, R'' is $\text{CH}_3\text{C(O)---}$.

- The invention will now be described by reference to the following examples and with reference to Figures 1 to 23 in which Figures 1 (a) to (d) are NMR spectra data, Figure 2 is IR spectra data, Figure 3 is GPC data and Figure 4 is DSC data of polymer precursor II according to the present invention; Figures 5 (a) to (d) are NMR spectra data, Figure 6 is IR spectra data and Figure 7 is GPC data of polymer precursor III according to the present invention; Figures 8 (a) to (d) are NMR spectra data, Figure 9 is IR spectra data, Figure 10 is GPC data of polymer precursor IV according to the present invention; Figure 11 is GPC data and Figure 12 is DSC data of polymer prepared in
- 20 Example 6 (a) according to the present invention; Figure 13 is GPC data, Figure 14 is DSC data and Figure 15 is NMR spectra data of polymer prepared in Example 6 (b) according to the present invention; Figure 16 is GPC data, Figure 17 is DSC data and Figure 18 is NMR spectra data of polymer prepared in Example 6 (c) according to the present invention; Figure 19 is GPC data and Figure 20 is NMR spectra data of polymer prepared in Example 6 (d) according to the present invention; and Figure 21 is GPC data, Figure 22 is DSC data and Figure 23 is NMR spectra data of polymer prepared in Example 6 (e) according to the present invention.

Preparation of Polymer Precursors

Example 1 : Preparation of Polymer Precursor I

- 30 $\text{HO(CH}_2\text{CH(OAc))}_x\text{(CH(OAc)CH}_2\text{)}_y\text{OH}$

This illustrates step (a) of the polymer precursor preparation process according to the present invention.

- Vinyl acetate and 1-propanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. A mixture of vinyl acetate (100 mL), hydrogen peroxide (60 mL, 27.5 wt. % solution in water) and 1-propanol (100 mL) were refluxed at 100°C for 3 days under nitrogen. 1-Propanol was then removed *in vacuo* and the resulting viscous oil was dissolved in dichloromethane. The solution was washed with water (3 x 100 mL) and dried over anhydrous magnesium sulphate.
- Dichloromethane was then removed under high vacuum and any remaining water removed by an azeotropic distillation using toluene.

The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 1055. The yield was about 30%.

- The polymer precursor was characterised by ^1H NMR, ^{13}C NMR and ^1H - ^{13}C correlation NMR and as well as by COSY, IR and GPC.

Example 2: Preparation of Polymer Precursor I



- This illustrates step (a) of the polymer precursor preparation process according to the present invention.

- Vinyl acetate and ethanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. A mixture of vinyl acetate (100 mL), hydrogen peroxide (60 mL, 27.5 wt. % solution in water) and ethanol (100 mL) were refluxed at 84°C for 8 days under nitrogen. Ethanol was then removed *in vacuo* and the resulting viscous oil was dissolved in dichloromethane. The solution was washed with water (3 x 100 mL) and dried over anhydrous magnesium sulphate. Dichloromethane was then removed under high vacuum and any remaining water removed by an azeotropic distillation using toluene.

- The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 1000. The number of OH equivalents determined twice by titration was 2.08 and 2.20. The yield was about 18%.

The polymer precursor was characterised by ^1H NMR, ^{13}C NMR and ^1H - ^{13}C correlation NMR and as well as by COSY, IR and GPC.

Example 3: Preparation of Polymer Precursor II

$\text{Br}(\text{Me})_2\text{CC}(\text{O})\text{O}(\text{CH}_2\text{CH}(\text{OAc}))_x(\text{CH}(\text{OAc})\text{CH}_2)_y\text{OC}(\text{O})\text{CMe}_2\text{Br}$.

5

This illustrates step (b) of the polymer precursor preparation process according to the present invention.

The polymer precursor I prepared in Example 2 (14.08 g, 15.3 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (5.20 mL, 37.3 mmol) under nitrogen. 2-Bromoisobutyryl bromide (4.20 mL, 34.0 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.

The polymer precursor was characterised by ^1H NMR (Figure 1(a)), ^{13}C pendants NMR (Figure 1(b)), COSY (Figure 1(c)) and ^1H - ^{13}C correlation NMR (Figure 1(d)), IR (Figure 2) and GPC (Figure 3). The compound prepared by the same method, but from a different batch was also characterised by DSC (Figure 4) (sample weight 1.000 mg).

TABLE 1 - Data for Figure 1(a) Example 3 (APJ 36)

NAME : Nov23-1998		EXPNO	: 30	PROCNO : 1
<u>F2 - Acquisition Parameters</u>				
5	Date	981123	Time	20.20
	INSTRUM	dpx300	RG	64
	PULPROG	zg30	DE	6.00 usec
	TD	32768	D1	1.00000000 sec
	SOLVENT	CDCl3	SF01	300.1318534 MHz
10	NS	16	NUC1	1H
	SWH	6172.839 Hz		
	AQ	2.6542580 sec		
<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz
15	WDW	EM	GB	0
<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm

TABLE 2 - Data for Figure 1(b) Example 3 (APJ 36)

NAME : Nov23-1998		EXPNO : 34		PROCNO : 1	
<u>F2 - Acquisition Parameters</u>					
5	Date	981123	Time	20.49	
	INSTRUM	dpx300	p2	50000000.00 usec	
	PULPROG	pendant	p4	50000000.00 usec	
	TD	65536	CNST2	500000.0000000	
	SOLVENT	CDCl3	d4	50000000.00000000 sec	
10	NS	128	d15	50000000.00000000 sec	
	SWH	18832.393 Hz	D1	500000.00000000 sec	
	AQ	1.7400308 sec	NUC2	1H	
	RG	4096	SF01	75.4763978 MHz	
	DE	6.00 usec	NUC1	13C	
15					
<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz	
	WDW	EM	GB	0	
<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm	

25

TABLE 3 - Data for Figure 1(c) Example 3 (APJ 36)

NAME : Nov23-1998 EXPNO : 31 PROCNO : 1			
<u>F2 - Acquisition Parameters</u>			
5	Date	981123	Time 20.21
	INSTRUM	dpx300	d0 0.00000300 sec
	PULPROG	cosygs	d13 0.00000300 sec
	TD	2048	D1 0.79888493 sec
	SOLVENT	CDCl3	SF01 300.1311641 MHz
10	NS	1	NUC1 1H
	SWH	2332.090 Hz	RG 32
	AQ	0.4391412 sec	DE 6.00 usec
<u>F1 - Acquisition Parameters</u>			
	NDO	1	FIDRES 9.109725 Hz
15	TD	256	SW 7.770 ppm
	SF01	300.1312 MHz	
<u>F2 - Processing Parameters</u>			
	SI	1024	LB 0.00 Hz
	WDW	SINE	GB 0
20	<u>F1-Processing Parameters</u>		
	SI	1024	SSB 0
	MC2	QF	LB 0.00 Hz
	SF	300.1300089 MHz	GB 0
	WDW	SINE	
25	<u>2D NMR plot parameters</u>		
	F2PPMCM	0.38851 ppm/cm	F2HZCM 116.60403 Hz/cm
	F1PPMCM	0.38851 ppm/cm	F1HZCM 116.60403 Hz/cm

TABLE 4 - Data for Figure 1(d) Example 3 (APJ 36)

	NAME : Nov23-1998		EXPNO : 33	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	981123	Time	20.30
	INSTRUM	dpx300	p2	50000000.00 sec
	PULPROG	inv4gs	d0	50000000.00000000 sec
	TD	1024	CNST2	500000.00000000
	SOLVENT	CDCI3	d2	50000000.00000000 sec
10	NS	2	d12	50000000.00000000 sec
	SWH	2495.010 Hz	d13	50000000.00000000 sec
	AQ	0.2052596 sec	d20	50000000.00000000 sec
	RG	13004	D1	500000.00000000 sec
	DE	6.00 usec	SF01	300.1307992 MHz
15	NUC1	1H	NUC2	13C
	<u>F1 - Acquisition Parameters</u>			
	NDO	2	FIDRES	130.643814 Hz
	TD	128	SW	221.562 ppm
	SF01	75.47522 MHz		
20	<u>F2 - Processing Parameters</u>			
	SI	2048	LB	0.00 Hz
	WDW	QSINE	GB	0
	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	5
25	MC2	QF	LB	0.00 Hz
	SF	75.4677190 MHz	GB	0
	WDW	QSINE		
	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.26816 ppm/cm	F2HZCM	80.48398 Hz/cm
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm

TABLE 5 - GPC ANALYSIS Figure 3 Example 3

	Sample name : apj182	Raw date filename : 24111.003
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one mixed E column and guard	Flow rate : 1.00 mL/min
	Detector : RI	
	<u>Data Processing :</u>	
	Method : 1	Calibration using : Narrow standards
10	Calibration limits : 5.75 to 11.22 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=11.557600, B = 1.747136, C = 0.119394, D = 0.003592	
	Last calibrated : Oct 20 14:17:10 1998	
	Flow rate marker : found at 11.23 in standards at 11.15 Mins.	
15	Broad peak start : 6.48 end : 10.27 Mins.	
	Standards	Sample
	K :	10.4000*10e-5
	alpha :	0.697
	<u>Molecular weight results :</u>	
20	Mp = 1745	Mn = 1128
	Mz = 3823	Mz+1 = 5989
	Polydispersity = 1.911	Peak area = 39878

Example 4 : Preparation of Polymer Precursor III

5 This illustrates step (a) of the polymer precursor preparation process according to the present invention.

Vinyl acetate and 1-propanol were deoxygenated by a stream of nitrogen for at least 30 minutes immediately prior to use. To a mixture of deoxygenated vinyl acetate (107.7 mL) and 1-propanol (200 mL) was added to the Azo initiator (Wako, VA-086) (2.8835g) having the formula :



The solution was refluxed under a nitrogen atmosphere overnight at 104°C. The initiator dissolved on warming. A biphasic solution was obtained on cooling the reaction mixture. The solvent was removed *in vacuo* and any remaining water removed by an azeotropic distillation using toluene.

15 From GPC, $M_n = 8930$ (using methyl methacrylate standards). Yield was 85 %.

The polymer precursor was characterised by ^1H NMR (Figure 5(a)), ^{13}C pendant NMR (Figure 5(b)), COSY (Figure 5(c)) and ^1H - ^{13}C correlation NMR (Figure 5(d)) as well as by IR (Figure 6) and GPC (Figure 7).

20

TABLE 6 - Data for Figure 5(a) Example 4 (APJ 14)

NAME : Feb08-1999		EXPNO	: 23	PROCNO : 1
<u>F2 - Acquisition Parameters</u>				
5	Date	990208	Time	23.27
	INSTRUM	dpx300	RG	128
	PULPROG	zg30	DE	6.00 usec
	TD	32768	D1	1.00000000 sec
	SOLVENT	CDCl3	SF01	300.1318534 MHz
10	NS	16	NUC1	1H
	SWH	6172.839 Hz		
	AQ	2.6542580 sec		
<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz
15	WDW	EM	GB	0
<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm

20

TABLE 7 - Data for Figure 5(b) Example 4 (APJ 14)

NAME : Feb08-1999		EXPNO : 22		PROCNO : 1	
<u>F2 - Acquisition Parameters</u>					
5	Date	990208	Time	23.25	
	INSTRUM	dpx300	p2	50000000.00 usec	
	PULPROG	pendant	p4	50000000.00 usec	
	TD	65536	CNST2	500000.0000000	
	SOLVENT	CDCl3	d4	50000000.00000000 sec	
10	NS	512	d15	50000000.00000000 sec	
	SWH	18832.393 Hz	D1	500000.00000000 sec	
	AQ	1.7400308 sec	NUC2	1H	
	RG	11585.2	SF01	75.4763978 MHz	
	DE	6.00 usec	NUC1	13C	
15					
<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz	
	WDW	EM	GB	0	
<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm	

TABLE 8 - Data for Figure 5(c) Example 4 (APJ 14)

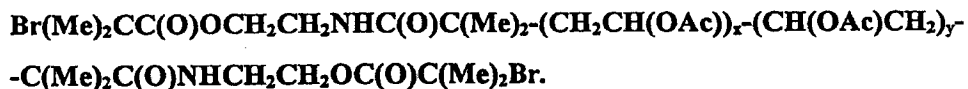
	NAME : Feb08-1999		EXPNO : 21		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	990208	Time	22.46		
	INSTRUM	dpx300	d0	0.00000300 sec		
	PULPROG	cosygs	d13	0.00000300 sec		
	TD	2048	D1	0.8234608 sec		
	SOLVENT	CDCI3	SF01	300.1311471 MHz		
10	NS	1	NUC1	1H		
	SWH	2480.159 Hz	RG	80.6		
	AQ	0.4129268 sec	DE	6.00 usec		
	<u>F1 - Acquisition Parameters</u>					
	NDO	1	FIDRES	9.688120 Hz		
15	TD	256	SW	8.264 ppm		
	SF01	300.1311 MHz				
	<u>F2 - Processing Parameters</u>					
	SI	1024	LB	0.00 Hz		
	WDW	SINE	GB	0		
20	<u>F1-Processing Parameters</u>					
	SI	1024	SSB	0		
	MC2	QF	LB	0.00 Hz		
	SF	300.1300236 MHz	GB	0		
	WDW	SINE				
25	<u>2D NMR plot parameters</u>					
	F2PPMCM	0.41318 ppm/cm	F2HZCM	124.00748 Hz/cm		
	F1PPMCM	0.41318 ppm/cm	F1HZCM	124.00748 Hz/cm		

TABLE 9 - Data for Figure 5(d) Example 4 (APJ 14)

NAME : Feb08-1999		EXPNO : 24		PROCNO : 1	
<u>F2 - Acquisition Parameters</u>					
5	Date	990208	Time	23.28	
	INSTRUM	dpx300	p2	50000000.00 sec	
	PULPROG	inv4gs	d0	50000000.00000000 sec	
	TD	1024	CNST2	500000.00000000	
	SOLVENT	CDCI3	d2	50000000.00000000 sec	
10	NS	2	d12	50000000.00000000 sec	
	SWH	2637.131 Hz	d13	50000000.00000000 sec	
	AQ	0.1942004 sec	d20	50000000.00000000 sec	
	RG	13004	D1	500000.00000000 sec	
	DE	6.00 usec	SF01	300.1310966 MHz	
15	NUC1	1H	NUC2	13C	
<u>F1 - Acquisition Parameters</u>					
	NDO	2	FIDRES	130.643814 Hz	
	TD	128	SW	221.562 ppm	
	SF01	75.47522 MHz			
20	<u>F2 - Processing Parameters</u>				
	SI	2048	LB	0.00 Hz	
	WDW	QSINE	GB	0	
<u>F1-Processing Parameters</u>					
	SI	1024	SSB	5	
25	MC2	QF	LB	0.00 Hz	
	SF	75.4677190 MHz	GB	0	
	WDW	QSINE			
<u>2D NMR plot parameters</u>					
	F2PPMCM	0.28344 ppm/cm	F2HZCM	85.06844 Hz/cm	
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm	

TABLE 10 - GPC ANALYSIS Figure 7 Example 4

	Sample name : apj	Raw data filename : 15072.002
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.83 to 17.98 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=18.699185, B = 2.346432, C = 0.135302, D = 0.003040	
	Last calibrated : Fri Jun 25 08:41:02 1999	
	Flow rate marker : found at 20.42 in standards at 20.37 Mins.	
15	Broad peak start : 11.22 end : 17.15 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19056	Mn = 7501 Mw = 19315
	Mz = 36240	Mz+1 = 53447 Mv = 17185
	Polydispersity = 2.575	Peak area = 25182

Example 5 : Preparation of Polymer Precursor IV

- 5 This illustrates step (b) of the polymer precursor preparation process according to the present invention. The polymer precursor III prepared in Example 4 (38.93 g, 4.36 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL) with triethylamine (1.46 mL, 10.46 mmol) under nitrogen. 2-Bromoisobutyryl bromide (1.29 mL, 10.5 mmol) was added dropwise with vigorous stirring at 0°C and the reaction mixture stirred
- 10 at room temperature overnight. The resulting precipitate was filtered off, the tetrahydrofuran removed *in vacuo* and the resulting viscous oil dissolved in dichloromethane. The solution was washed with saturated hydrogen carbonate (3 x 50 mL), dried over anhydrous magnesium sulphate and the dichloromethane removed under high vacuum to give a bright orange oil.
- 15 The polymer precursor was characterised by ¹H NMR (Figure 8(a)), ¹³C pendant NMR (Figure 8(b)), COSY (Figure 8(c)) and ¹H- ¹³C correlation NMR (Figure 8(d)) as well as by IR (Figure 9) and GPC (Figure 10).

TABLE 11 - Data for Figure 8(a) Example 5 (APJ 58)

NAME : Mar17-1999		EXPNO	: 10	PROCNO : 1
<u>F2 - Acquisition Parameters</u>				
5	Date	990317	Time	23.02
	INSTRUM	dpx300	RG	32
	PULPROG	zg30	DE	6.00 usec
	TD	32768	D1	1.00000000 sec
	SOLVENT	CDCl3	SF01	300.1318534 MHz
10	NS	16	NUC1	1H
	SWH	6172.839 Hz		
	AQ	2.6542580 sec		
<u>F2 - Processing Parameters</u>				
	SI	32768	LB	-0.20 Hz
15	WDW	EM	GB	0
<u>1D NMR plot parameters</u>				
	PPMCM	0.25641 ppm/cm	HZCM	76.95641 Hz/cm

TABLE 12 - Data for Figure 8(b) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 12		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	990317	Time	23.42		
	INSTRUM	dpx300	p2	50000000.00 usec		
	PULPROG	pendant	p4	50000000.00 usec		
	TD	65536	CNST2	500000.0000000		
	SOLVENT	CDCl3	d4	50000000.00000000 sec		
10	NS	512	d15	50000000.00000000 sec		
	SWH	18832.393 Hz	D1	500000.00000000 sec		
	AQ	1.7400308 sec	NUC2	1H		
	RG	7298.2	SF01	75.4763978 MHz		
	DE	6.00 usec	NUC1	13C		
15						
	<u>F2 - Processing Parameters</u>					
	SI	32768	LB	2.00 Hz		
	WDW	EM	GB	0		
	<u>1D NMR plot parameters</u>					
20	PPMCM	5.64103 ppm/cm	HZCM	425.71533 Hz/cm		

TABLE 13 - Data for Figure 8(c) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 11	PROCNO : 1
	<u>F2 - Acquisition Parameters</u>			
5	Date	990317	Time	23.03
	INSTRUM	dpx300	d0	0.00000300 sec
	PULPROG	cosygs	d13	0.00000300 sec
	TD	2048	D1	0.79683691 sec
	SOLVENT	CDC13	SF01	300.1311718 MHz
10	NS	1	NUC1	1H
	SWH	2332.090 Hz	RG	16
	AQ	0.4391412 sec	DE	6.00 usec
	<u>F1 - Acquisition Parameters</u>			
	NDO	1	FIDRES	9.109725 Hz
15	TD	256	SW	7.770 ppm
	SF01	300.1312 MHz		
	<u>F2 - Processing Parameters</u>			
	SI	1024	LB	0.00 Hz
	WDW	SINE	GB	0
20	<u>F1-Processing Parameters</u>			
	SI	1024	SSB	0
	MC2	QF	LB	0.00 Hz
	SF	300.1299922 MHz	GB	0
	WDW	SINE		
25	<u>2D NMR plot parameters</u>			
	F2PPMCM	0.38851 ppm/cm	F2HZCM	116.60403 Hz/cm
	F1PPMCM	0.38851 ppm/cm	F1HZCM	116.60403 Hz/cm

TABLE 14 - Data for Figure 8(d) Example 5 (APJ 58)

	NAME : Mar17-1999		EXPNO : 14		PROCNO : 1	
	<u>F2 - Acquisition Parameters</u>					
5	Date	990317	Time	23.46		
	INSTRUM	dpx300	p2	50000000.00 sec		
	PULPROG	inv4gs	d0	50000000.00000000 sec		
	TD	1024	CNST2	500000.00000000		
	SOLVENT	CDCl3	d2	50000000.00000000 sec		
10	NS	2	d12	50000000.00000000 sec		
	SWH	2653.928 Hz	d13	50000000.00000000 sec		
	AQ	0.1929716 sec	d20	50000000.00000000 sec		
	RG	6502	D1	500000.00000000 sec		
	DE	6.00 usec	SF01	300.1310520 MHz		
15	NUC1	1H	NUC2	13C		
	<u>F1 - Acquisition Parameters</u>					
	NDO	2	FIDRES	130.643814 Hz		
	TD	128	SW	221.562 ppm		
	SF01	75.47522 MHz				
20	<u>F2 - Processing Parameters</u>					
	SI	2048	LB	0.00 Hz		
	WDW	QSINE	GB	0		
	<u>F1-Processing Parameters</u>					
	SI	1024	SSB	5		
25	MC2	QF	LB	0.00 Hz		
	SF	75.4677190 MHz	GB	0		
	WDW	QSINE				
	<u>2D NMR plot parameters</u>					
	F2PPMCM	0.28524 ppm/cm	F2HZCM	85.61028 Hz/cm		
30	F1PPMCM	11.07808 ppm/cm	F1HZCM	836.03729 Hz/cm		

TABLE 15 - GPC ANALYSIS Figure 10 Example 5

	Sample name : aj1114	Raw date filename : 25062.002
	<u>Conditions :</u>	
5	Solvent : THF	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.80 to 17.93 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=18.699185, B = 2.346432, C = 0.135302, D = 0.003040	
	Last calibrated : Fri Jun 25 08:41:02 1999	
	Flow rate marker : found at 20.35 in standards at 20.37 Mins.	
15	Broad peak start : 11.15 end : 16.97 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19699	Mn = 9183 Mw = 20468
	Mz = 35738	Mz+1 = 51313 Mv = 18502
	Polydispersity = 2.229	Peak area = 25866

25 **Atom transfer polymerisation of vinyl monomers using α, ω difunctional polymer precursors**

Preparation of organodiimine ligands

Preparation of N-propyl-pyridinal methanimine

30 To a solution of pyridine-2-carboxaldehyde (1.78 mL, 1.87×10^{-2} mol) and diethyl ether (30 mL) was added n-propylamine (1.55 mL, 1.88×10^{-2} mol). The reaction mixture was stirred for 10 minutes at room temperature prior to addition of anhydrous magnesium sulphate and stirring for a further 30 minutes. The magnesium

sulphate was removed by filtration, and volatiles were removed under reduced pressure to give the product in quantitative yield as a pale yellow oil.

¹H NMR (CDCl₃, 373 K, 400.13 MHz): d = 8.51 (d, *J* = 3.5 Hz, 1H) 8.26 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 4.6 Hz, 1H), 3.52 (t, *J* = 7.6 Hz, 2H), 1.63 (sext, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.5 Hz, 3H). ¹³C (CDCl₃, 373K, 100.61 MHz): d = 161.51, 154.44, 149.18, 136.28, 124.37, 120.97, 63.08, 23.65, 11.65 ppm. IR (NaCl, film), 3053-2830, 1648, 1587, 1566, 772, 742 cm⁻¹. Bp = 218°C.

Preparation of N-octyl-pyridinal methanimine.

To a solution of pyridine-2-carboxaldehyde (19 mL, 0.20 mol) and diethyl ether (150 mL) in a 250 mL round-bottomed flask was added octylamine (33.9 mL, 0.20 mol). The reaction mixture was stirred for 1 hour prior to addition of anhydrous magnesium sulphate (25.2 g) and stirring for a further 2 hours. The magnesium sulphate was removed by filtration and was washed with diethyl ether. The ether was subsequently removed by rotary evaporation to give a dark yellow viscous liquid. The liquid was fractionally distilled at 96 °C at 0.04 torr to give a pale yellow liquid. Yield = 40.5 g (90.5%). ¹H NMR (CDCl₃, 298 K, 250.13 MHz) d = 8.60 (d, *J* = 4.9 Hz, 1H) 8.33 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 6.2 Hz, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 1.68 (m, *J* = 7.0 Hz, 2H), 1.26 (m, *J* = 7.3 Hz, 10H), 0.82 (t, *J* = 7.0 Hz, 3H). ¹³C (CDCl₃, 298K, 100.16 MHz): 161.1, 154.5, 148.8, 135.7, 123.9, 120.5, 61.1, 31.5, 30.4, 29.1, 28.9, 27.0, 22.3, 13.7. Anal. Calc. for C₁₄H₂₂N₂: C = 77.01, H = 10.16, N = 12.82. Found C = 77.15, H = 10.25, N = 12.85.

General procedure for atom transfer polymerisation.

Monomers were passed down a basic alumina column (Aldrich, Brockmann I grade) immediately prior to use, degassed by a stream of nitrogen for at least 30 minutes and freeze-pump-thawed (three times). Solvents were deoxygenated by a stream of nitrogen for at least 30 minutes prior to use. Cu(I)Br was purified according to a published procedure (Keller, R.N. and Wcycoff, M.D. Inorg. Synth. 1947, 2,1.). All atom transfer polymerisation experiments carried out at 90°C except for those involving styrene which were heated to 110°C. A slight excess of ligand (10%) is added to the reaction mixture.

The atom transfer polymerisation experiments have been carried out using slightly varying methods.

Example 6 : Polymerisation of methyl methacrylate with polymer precursor II.

- Polymer precursor, initiator, prepared in Example 3 (1.48 g, 1.0 mmol) and a magnetic follower were placed in a Schlenk tube. Toluene (10.70 mL), N-octyl-pyridinal methanimine (0.96 g, 4.2 mmol) prepared as hereinbefore described and monomer
- 5 (methyl methacrylate) (5.34 mL) were added. The solution was deoxygenated via three freeze-pump-thaw cycles and added to Cu(I)Br (0.286g, 2.0 mmol). Reaction mixture subsequently heated to 90°C or 110°C depending on the monomer used. Samples were removed by syringe periodically (every 30 minutes) for analysis (GPC and gravimetrically). All molecular weight data was recorded on un-precipitated polymer.
- 10 The final polymer solution was passed down a basic alumina column and precipitated into n-pentane.

This illustrates preparation of a block polymer according to the present invention using a molar ratio of ratio of monomer : polymer precursor : metal : ligand of 100:1:2:4 in 66% toluene solution. The reaction was terminated at about 96% conversion.

- 15 The molecular number Mn was determined by GPC using methyl methacrylate standards to be about 27340 (Figure 11).

TABLE 16 - GPC ANALYSIS Figure 11 Example 6(a)

	Sample name : aj1789	Raw date filename : 02112.017
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 10.00 to 20.65 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	$A=11.819727, B = 0.759678, C = 0.016374, D = 0.000144$	
	Last calibrated : Wed Oct 21 10:54:26 1998	
	Flow rate marker : found at 20.67 in standards at 20.38 Mins.	
15	Broad peak start : 11.08 end : 15.08 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 35898	Mn = 27342 Mw = 41579
	Mz = 58673	Mz+1 = 76178 Mv = 39238
	Polydispersity = 1.521	Peak area = 5112

The polymer precursor was also characterised by DSC (Figure 12) (3.000 mg sample weight Total Mn - 33000 heat from -50.00°C to 140.00°C at 20.00°C/min).

This example (Example 6(a)) was repeated using different monomers and different molar ratios of reagents as follows :

Example 6 (b) : The monomer used was methyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 50 : 1 : 2 : 4.

Product Mn = 14490 using poly(methyl methacrylate) standard for GPC (Figure 13).

TABLE 17 - GPC ANALYSIS Figure 13 Example 6(b)

	Sample name : aj1569	Raw date filename : 02112.026
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.97 to 20.60 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=11.819727, B = 0.759678, C = 0.016374, D = 0.000144	
	Last calibrated : Wed Oct 21 10:54:26 1998	
	Flow rate marker : found at 20.62 in standards at 20.38 Mins.	
15	Broad peak start : 11.58	end : 15.78 Mins.
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 19651	Mn = 14489 Mw = 21615
	Mz = 30835	Mz+1 = 41305 Mv = 20405
	Polydispersity = 1.492	Peak area = 6773

The polymer precursor was also characterised by DSC (Figure 14) (sample weight 8.100 mg , Total Mn - 17000, heat from -60.00°C to 140.00°C at 20.00°C/min.) and by ¹H NMR in CDCl₃ (Figure 15).

Example 6 (c) : The monomer used was styrene.

Molar ratio of monomer : polymer precursor : metal : ligand = 100 : 1 : 2 : 4.

Product Mn = 16440 using poly(styrene) standard for GPC (Figure 16).

TABLE 18 - GPC ANALYSIS Figure 16 Example 6(c)

	Sample name : apj1669		Raw date filename : 29102.009	
	<u>Conditions :</u>			
5	Solvent :	THF with toluene	Temperature : room temp.	
	Column set :	one guard column and 2 mixed D	Flow rate : 1.00 mL/min	
	Detector :	DRI/UV		
	<u>Data Processing :</u>			
	Method :	21 Calibration using : Narrow standards		
10	Calibration limits :	9.58 to 20.67 Mins		
	Curve used :	3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³	
		A=13.147278, B = 1.020344, C = 0.032583, D = 0.000469		
	Last calibrated :	Wed Oct 21 11:04:12 1998		
	Flow rate marker :	found at 20.67 in standards at 20.40 Mins.		
15	Broad peak start :	11.52	end : 15.85 Mins.	
		Standards	Sample	
	K :	10.4000*10e-5	10.4000* 10e-5	
	alpha :	0.700	0.700	
	<u>Molecular weight results :</u>			
20	Mp = 24042	Mn = 16442	Mw = 24927	
	Mz = 35106	Mz+1 = 45798	Mv = 23556	
	Polydispersity = 1.516	Peak area = 7693		

The polymer precursor was also characterised by DSC (Figure 17) (1.00 mg sample weight, total Mn - 17000, heat from -50.00°C to 140.00°C at 20.00°C/min) and by ¹H NMR CDCl₃ (Figure 18).

Example 6 (d) : The monomer used was n-butyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 100 : 1 : 2 : 4.

Product Mn = 13190 using poly(methyl methacrylate) standard for GPC (Figure 19).

30

TABLE 19 - GPC ANALYSIS Figure 19 Example 6(d)

	Sample name : apj188 11	Raw date filename : 01122.038
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 2 Calibration using : Narrow standards	
10	Calibration limits : 9.88 to 20.42 Mins	
	Curve used : 3 rd order polynomial	Coefficients : $\text{Log}(M) = A + BT + CT^2 + DT^3$
	A=11.821880, B = 0.759705, C = 0.016359, D = 0.000144	
	Last calibrated : Sun Nov 15 11:08:30 1998	
	Flow rate marker : found at 20.43 in standards at 20.38 Mins.	
15	Broad peak start : 11.23 end : 16.10 Mins.	
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 17626	Mn = 13190 Mw = 21880
	Mz = 33488	Mz+1 = 47717 Mv = 20421
	Polydispersity = 1.659	Peak area = 2996

The polymer precursor was also characterised by ¹H NMR in CDCl₃ (Figure 20).

25 Example 6 (e) : The monomer used was n-butyl methacrylate.

Molar ratio of monomer : polymer precursor : metal : ligand = 50 : 1 : 2 : 4.

Product Mn = 8490 using poly(methyl methacrylate) standard for GPC (Figure 21).

TABLE 20 - GPC ANALYSIS Figure 21 Example 6(e)

	Sample name : apj188 30	Raw date filename : 01122.048
	<u>Conditions :</u>	
5	Solvent : THF with toluene	Temperature : room temp.
	Column set : one guard column and 2 mixed D	Flow rate : 1.00 mL/min
	Detector : DRI/UV	
	<u>Data Processing :</u>	
	Method : 2	Calibration using : Narrow standards
10	Calibration limits : 9.88 to 20.42 Mins	
	Curve used : 3 rd order polynomial	Coefficients : Log(M) = A + BT + CT ² + DT ³
	A=11.821880, B = 0.759705, C = 0.016359, D = 0.000144	
	Last calibrated : Sun Nov 15 11:08:30 1998	
	Flow rate marker : found at 20.42 in standards at 20.38 Mins.	
15	Broad peak start : 11.83	end : 16.55 Mins.
	Standards	Sample
	K : 10.4000*10e-5	10.4000* 10e-5
	alpha : 0.697	0.697
	<u>Molecular weight results :</u>	
20	Mp = 12694	Mn = 8486 Mw = 13647
	Mz = 20030	Mz+1 = 27335 Mv = 12805
	Polydispersity = 1.608	Peak area = 6699

The polymer precursor was also characterised by DSC (Figure 22) (sample weight 3.200 mg, heat from -50.00°C to 120.00°C at 20.00°C/min) and by ¹H NMR in CDCl₃ (Figure 23).

Example 7: Polymerisation of styrene with polymer precursor IV.

Polymer precursor IV prepared in Example 5 (1.1044 g, 0.4 mmol), Cu(I)Br (0.1139 g, 0.8 mmol) and a magnetic follower were placed in a Schlenk tube. Deoxygenated toluene(4.40 mL) and N-propyl-2-pyridinal methanimine (0.26 g, 1.76 mmol) prepared as hereinbeforedescribed were added and the solution heated to 110°C.

Deoxygenated inhibitor free styrene (4.40 mL) was then added ($t = 0$). Samples were removed periodically for analysis, via syringe. All molecular weight data recorded on un-precipitated polymer. The final polymer solution was passed down a basic alumina column and precipitated into n-pentane.

- 5 This illustrates preparation of a block polymer according to the present invention using a molar ratio of monomer : polymer precursor : metal : ligand of 100 : 1 : 2 : 4 in 50% to toluene solution.

10

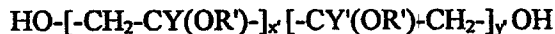
15

Claims :

1. A process for the preparation of a block polymer which process comprises a transition metal mediated, atom transfer polymerisation of an ethylenically unsaturated monomer with an α, ω di-functional polymer precursor having repeating units derived from an ethylenically unsaturated carboxylate.
- 5 2. A process as claimed in claim 1 wherein the ethylenically unsaturated carboxylate is vinyl acetate.
3. A process as claimed in claim 1 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
- 10 4. A process as claimed in claim 2 wherein the ethylenically unsaturated monomer is selected from the group consisting of styrene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, unsubstituted acrylate and methacrylate.
5. An α, ω di-functional polymer precursor having a molecular weight in the range from 500 to 50000 and being represented by the formula :

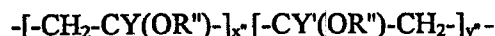
15
$$X-[-CH_2-CY(OR)-]_x-[-CY'(OR)-CH_2-]_y-X'$$
 wherein x and y are integers independently greater than 1; Y and Y' are independently H or $-CH_3$; R represents a hydrocarbyl group; and X and X' independently represent substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.
- 20 6. A polymer precursor as claimed in claim 5 wherein R is selected from the group consisting of $CH_3C(O)-$, $Y''-C(O)-$, $PhC(O)-$, $Ph-$, $PhCH_2-$,

- CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_zC(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F.
- 5 7. A polymer precursor as claimed in claim 5 wherein R is CH₃C(O)-.
8. A process for the production of an α, ω di-functional polymer precursor which process comprises the steps of :
- (a) reacting an ethylenically unsaturated carboxylate with a radical initiator having a substitutable functional group; and
- 10 (b) substituting the functional groups on the product of step (a) with substituents active for the formation of block polymers in a transition metal mediated, atom transfer polymerisation process.
9. A process as claimed in claim 8 wherein the ethylenically unsaturated carboxylate is vinyl acetate.
- 15 10. A polymer precursor having a molecular weight in the range from 500 to 50000, preferably from 1000 to 20000 and being represented by the formula :



- wherein x' and y' are integers independently greater than 1; Y and Y' are independently H or -CH₃; and R' represents a hydrocarbyl group.
- 20 11. A polymer precursor as claimed in claim 10 wherein R' is selected from the group consisting of CH₃C(O)-, Y"-C(O)-, PhC(O)-, Ph-, PhCH₂-,

- CH₃-(CH₂-CH₂-CH₂-CH₂)_zC(O)-, CH₃-(CH₂-CH=CH-CH₂)_zC(O)- and substituted phenyl; wherein Y" is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is an integer up to 5000, z" is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO₂, OMe, CN, NMe₂, OH, Cl, Br, and F.
- 25 12. A polymer precursor as claimed in claim 10 wherein R' is CH₃C(O)-.
13. A block polymer comprising alternating repeating units of -[A]- and -[B]- in which -A- represents a polymer block having a molecular weight in the range from 500 to 50000 and being represented by the formula :
- 30



wherein x'' and y'' are integers independently greater than 1; Y and Y' are independently H or $-\text{CH}_3$ and R'' represents a hydrocarbyl group and $-\text{B}-$ represents at least one polymer repeating unit selected from the group consisting of acrylic, substituted acrylic, methacrylic, substituted methacrylic, acrylonitrile, methacrylonitrile, acylamide,

5 methacrylamide and styrenic polymer units.

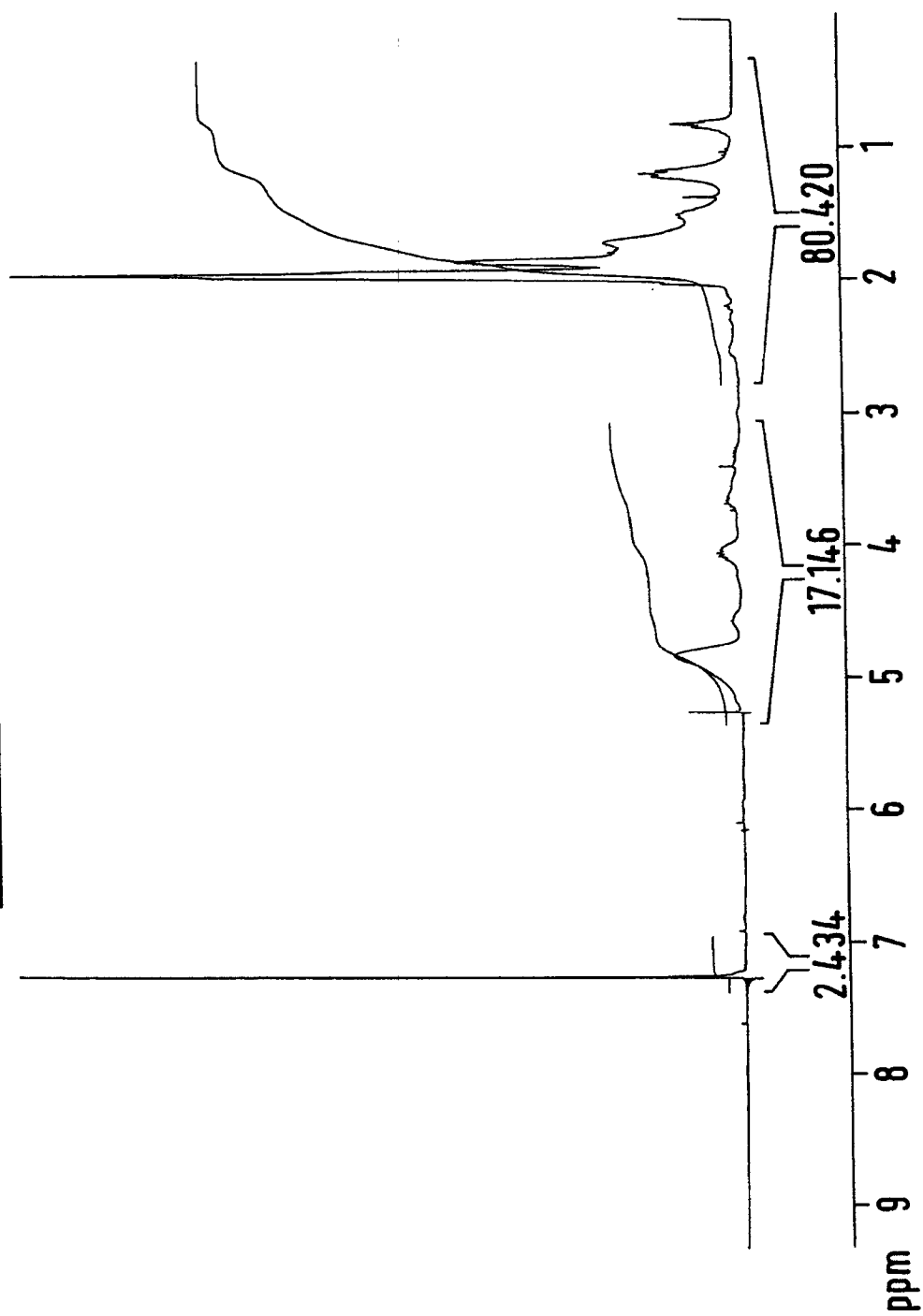
14. A block polymer as claimed in claim 13 wherein R'' is selected from the group consisting of $\text{CH}_3\text{C}(\text{O})-$, $\text{Y}''-\text{C}(\text{O})-$, $\text{PhC}(\text{O})-$, $\text{Ph}-$, PhCH_2- , $\text{CH}_3-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_{z'}\text{C}(\text{O})-$, $\text{CH}_3-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_{z'}\text{C}(\text{O})-$ and substituted phenyl; wherein Y'' is an n-alkyl group having up to 18 carbon atoms, Ph is phenyl, z' is

10 an integer up to 5000, z'' is an integer up to 5000 and the substituted phenyl is substituted with at least one substituent selected from the group consisting of NO_2 , OMe, CN, NMe_2 , OH, CL, Br, and F.

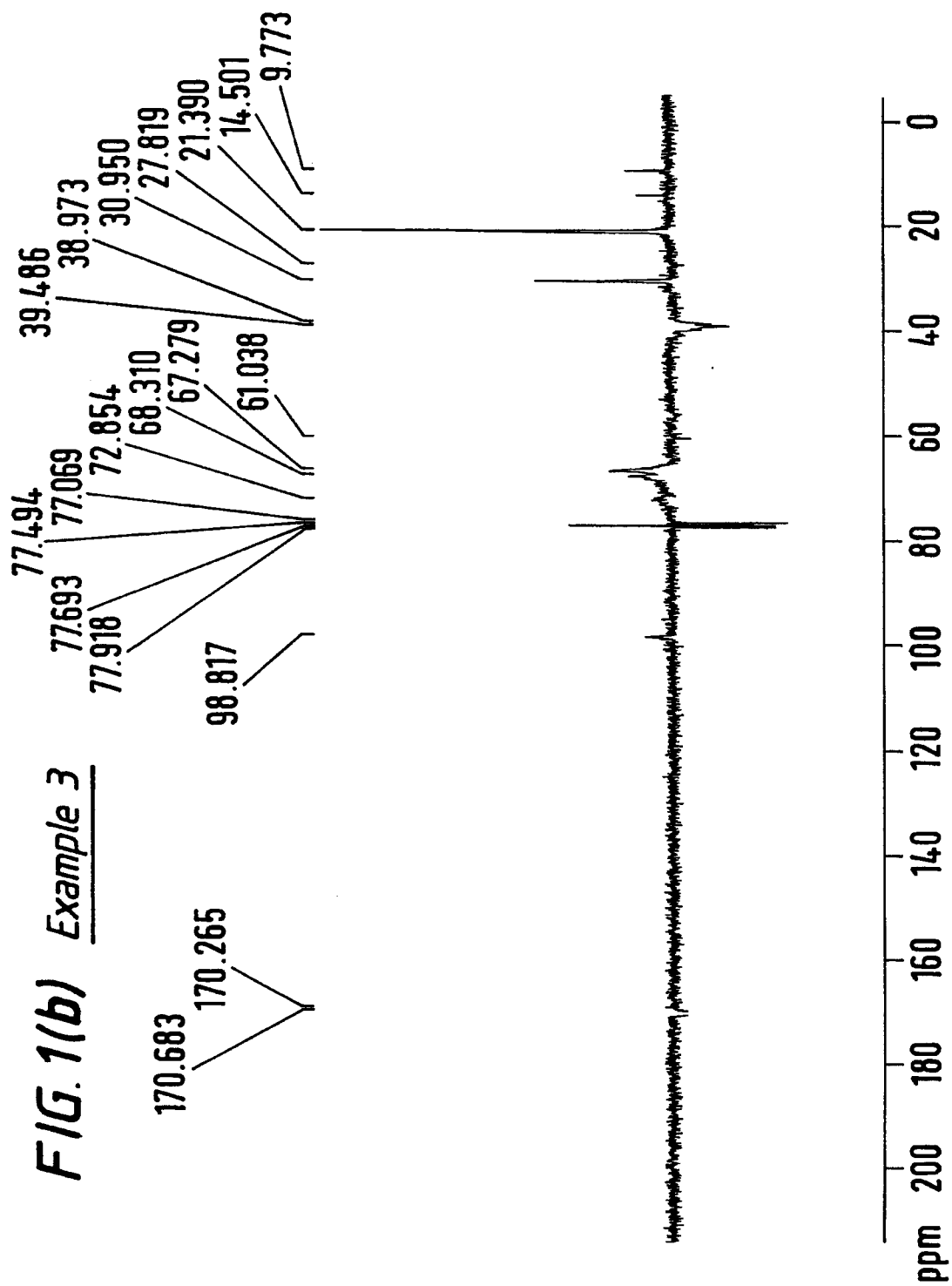
15. A polymer precursor as claimed in claim 13 wherein R'' is $\text{CH}_3\text{C}(\text{O})-$.

15

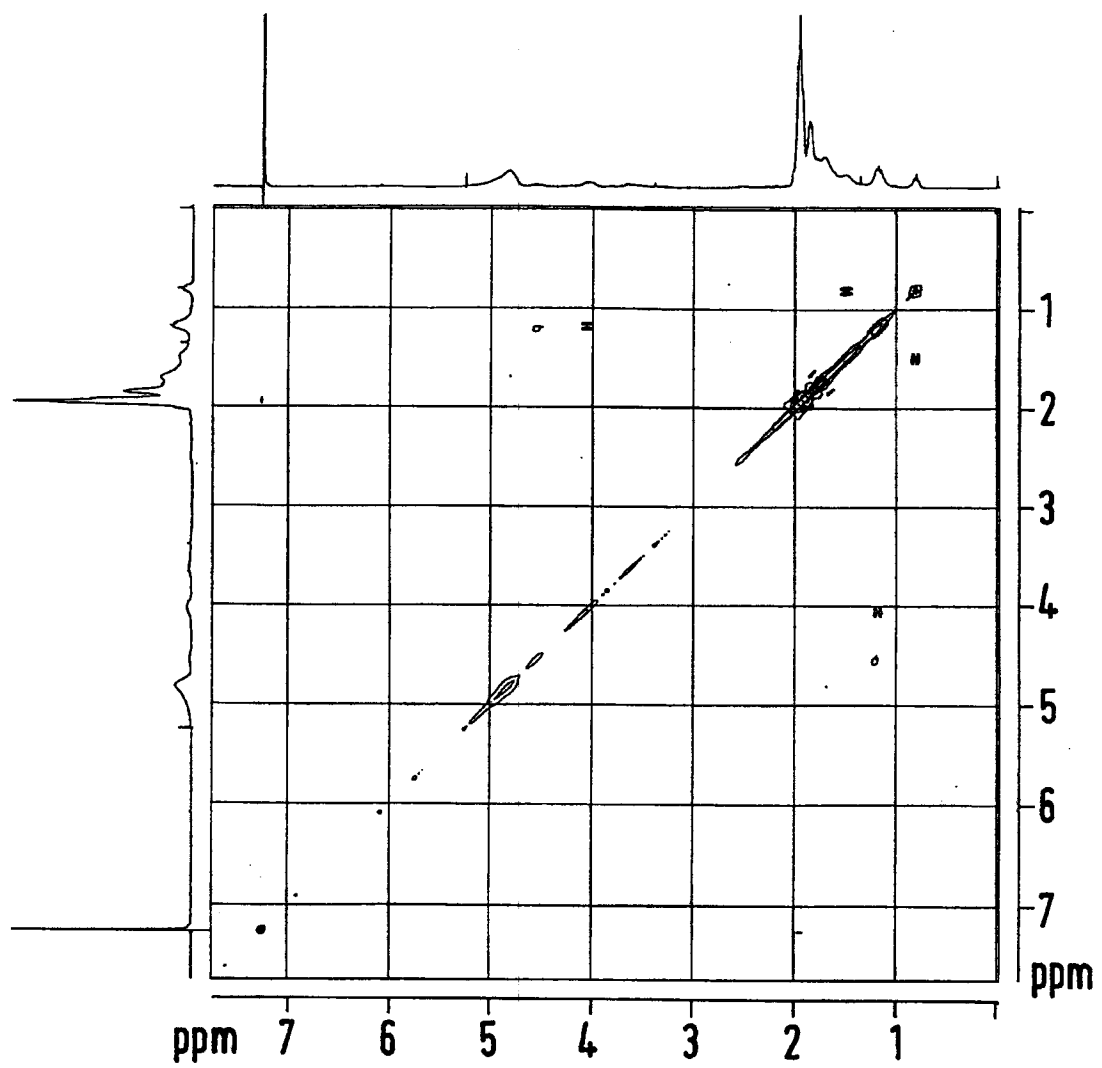
1/34

FIG. 1(a) Example 3

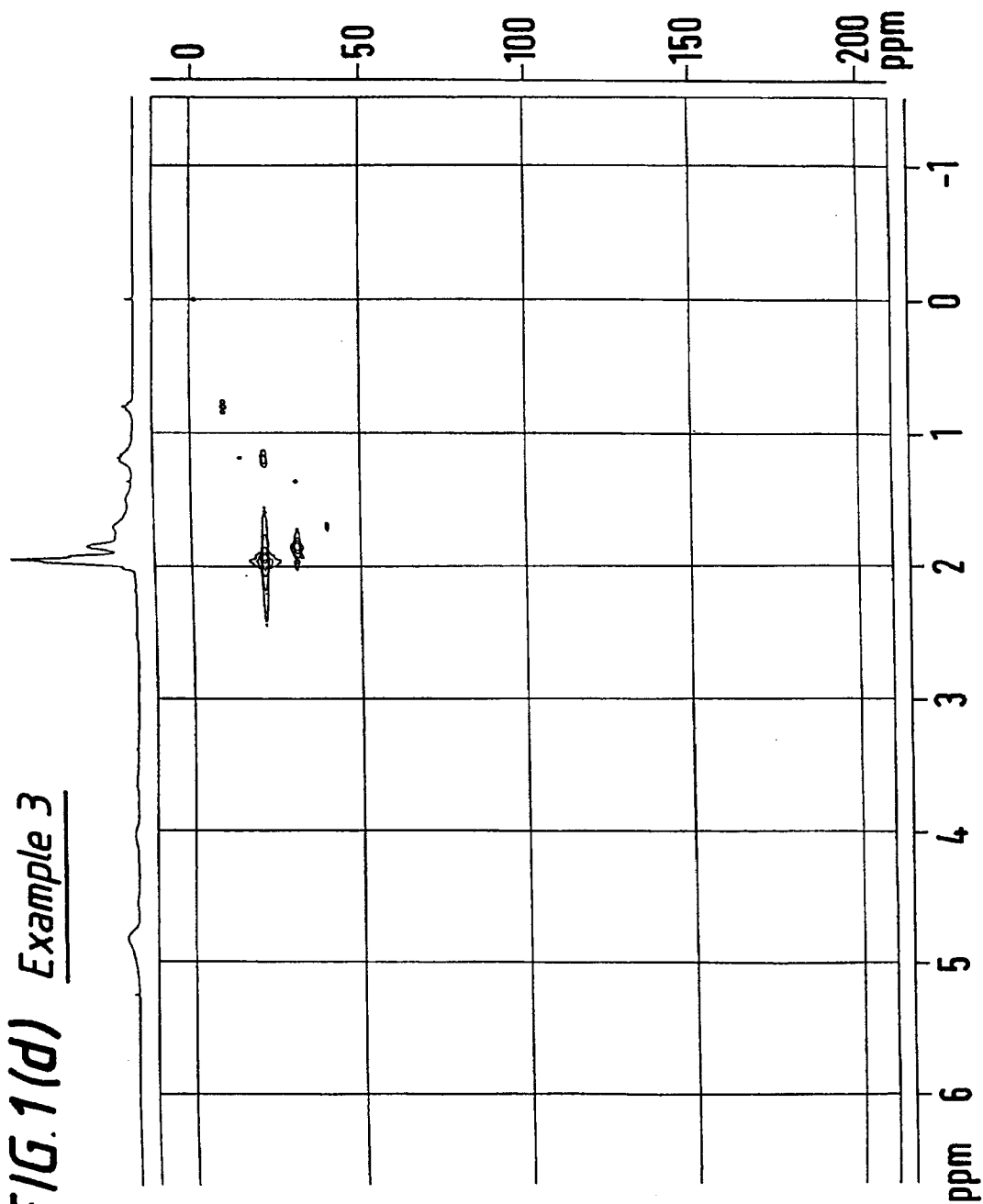
2/34



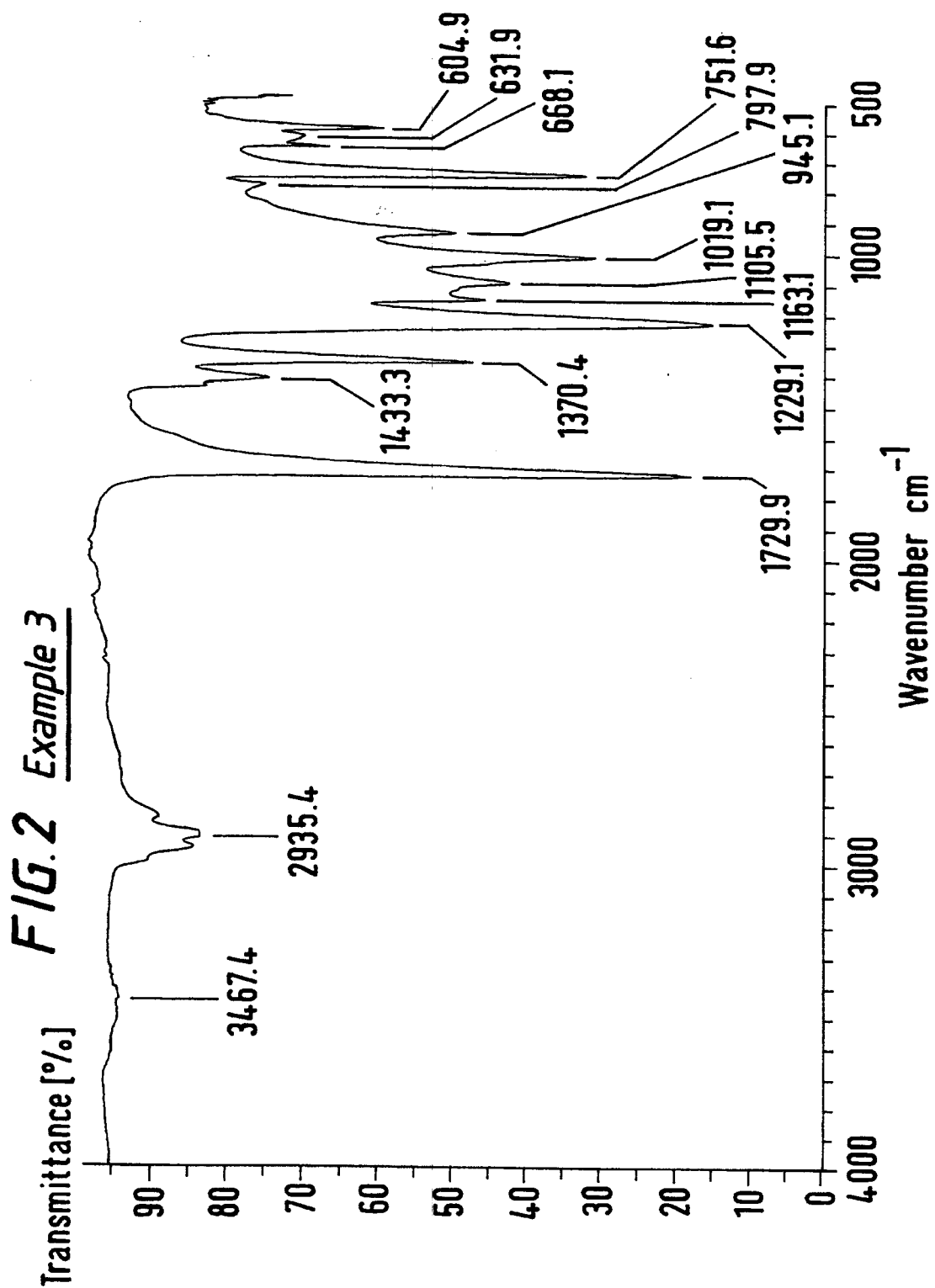
3/34

FIG. 1(c) Example 3

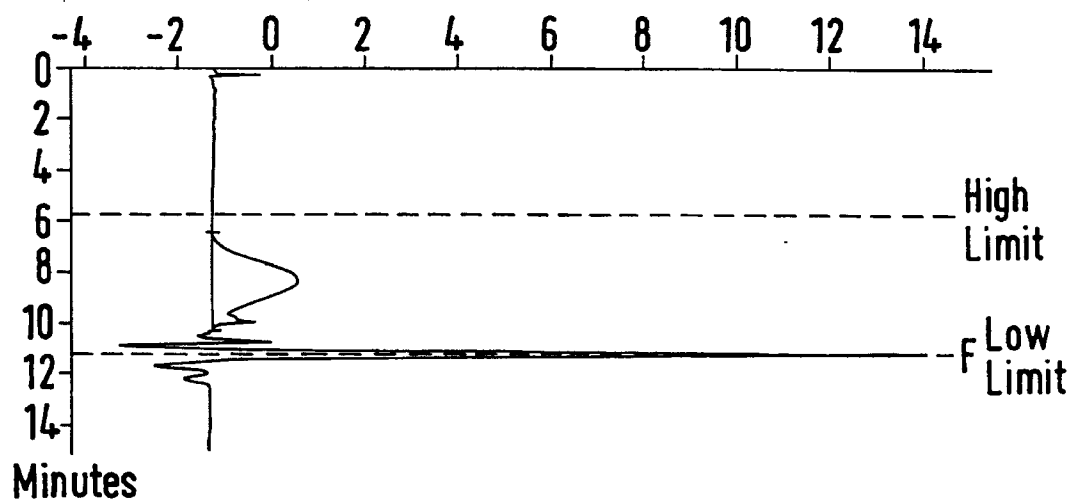
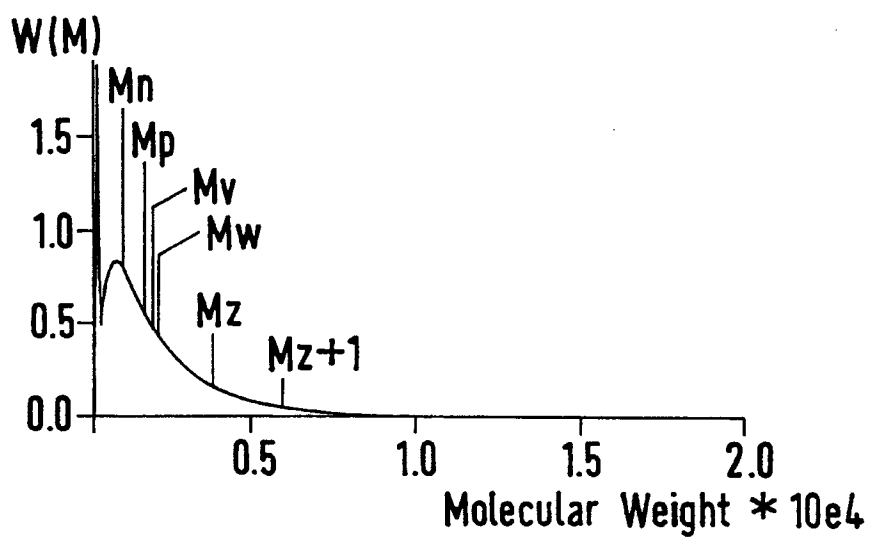
4/34

FIG. 1(d) Example 3

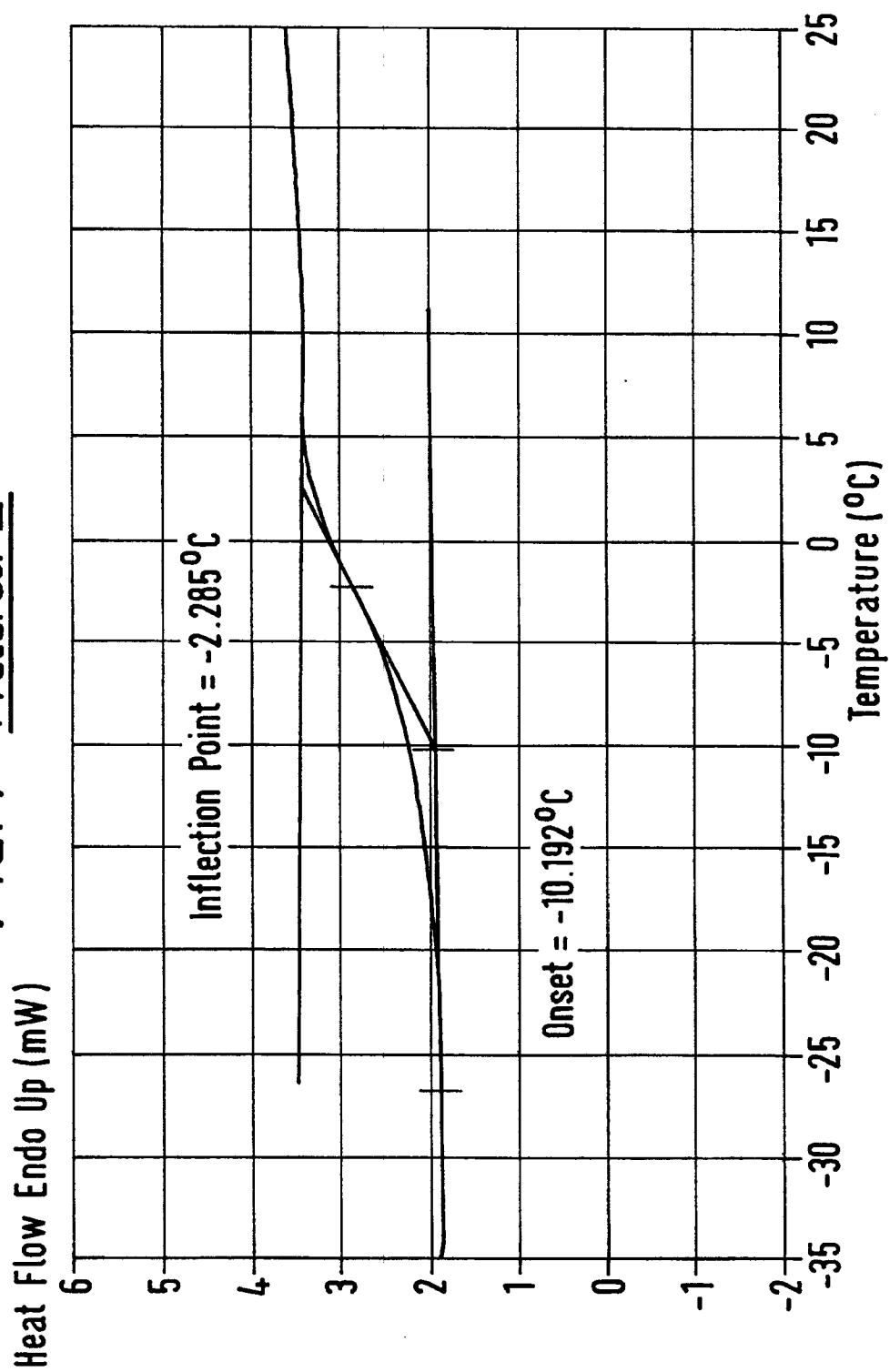
5/34



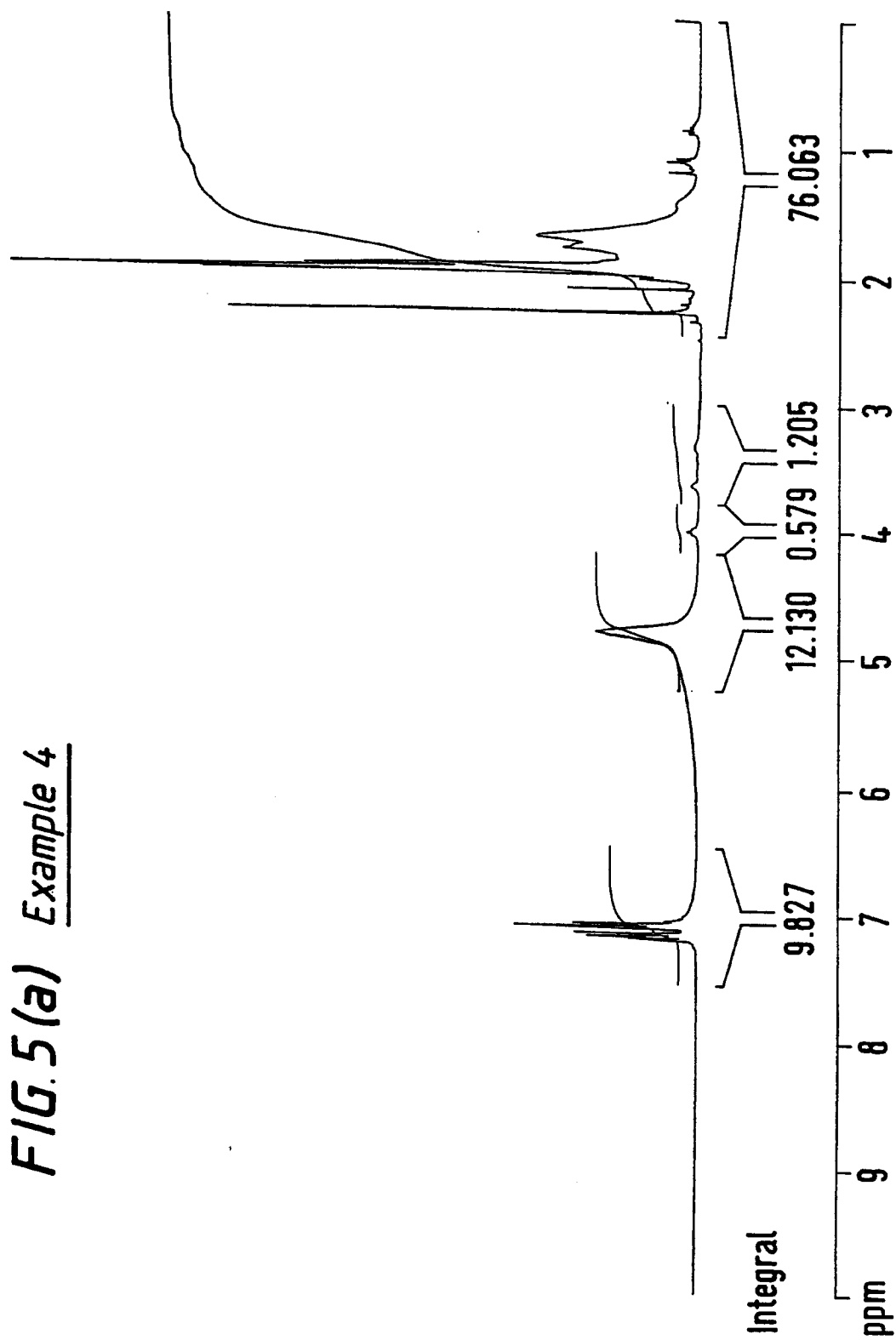
6/34

FIG.3 Example 3*Raw Chromatogram:**W(M) plot:*

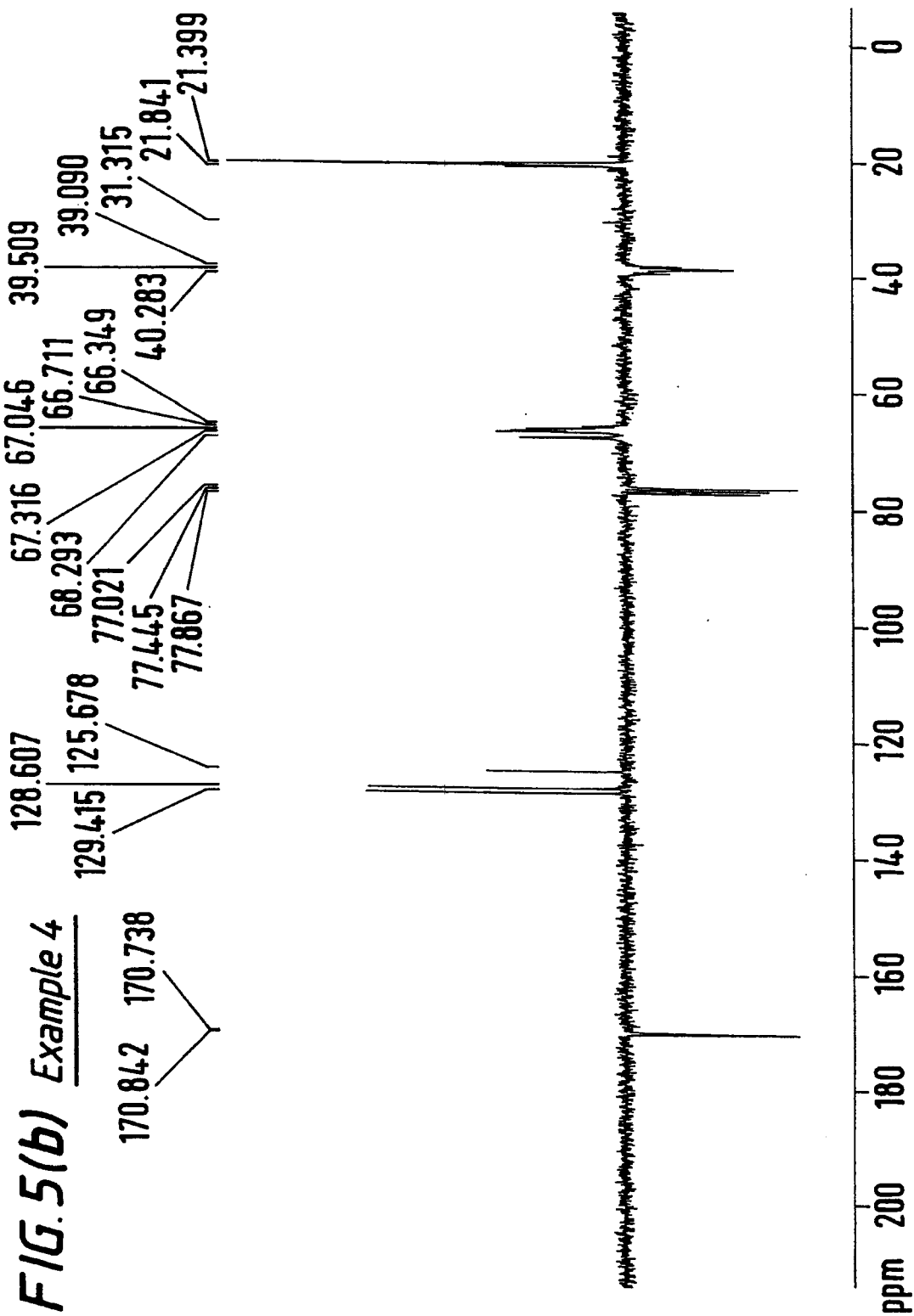
7/34

FIG. 4 Precursor II

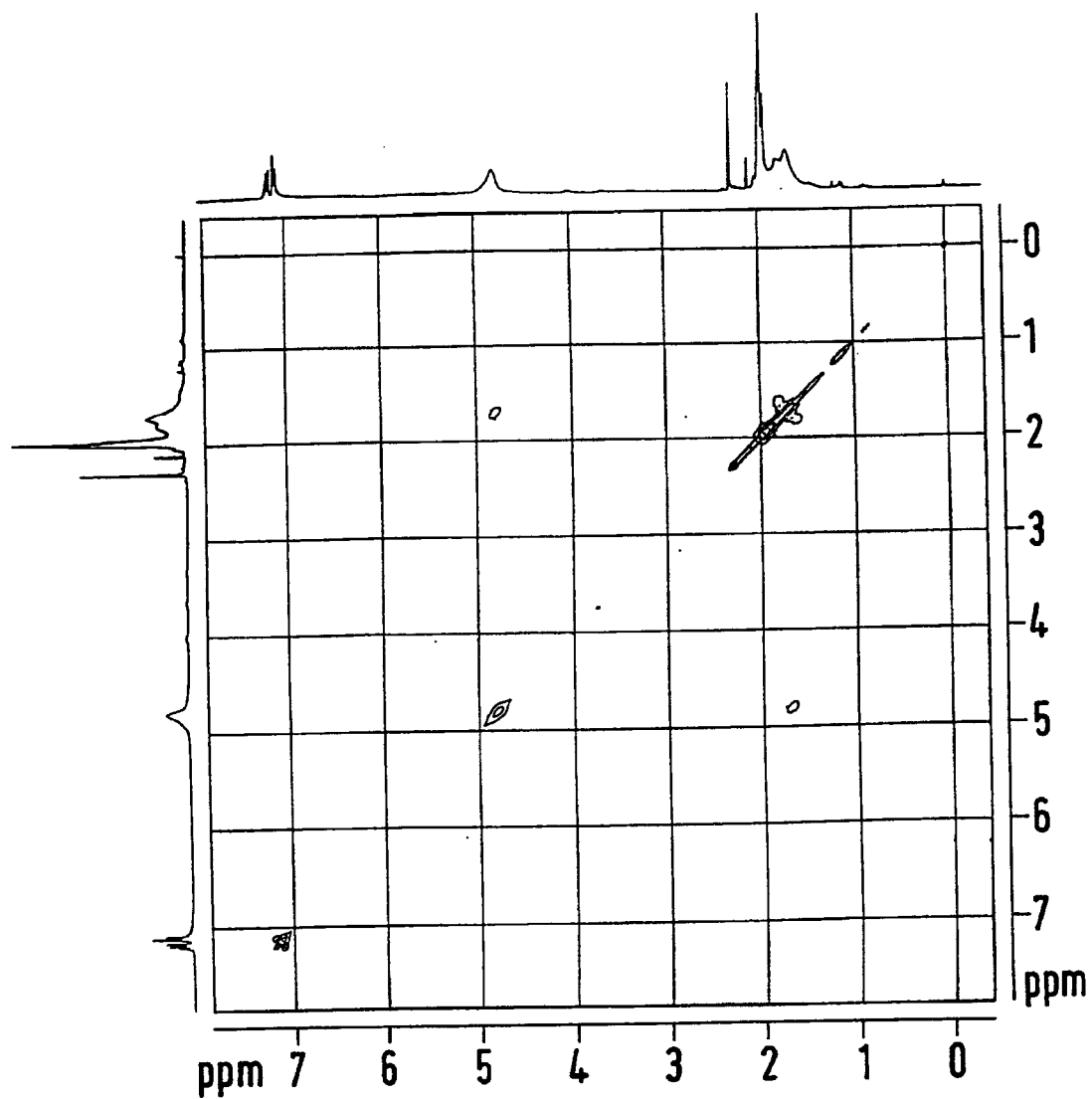
8/34

FIG. 5(a) Example 4

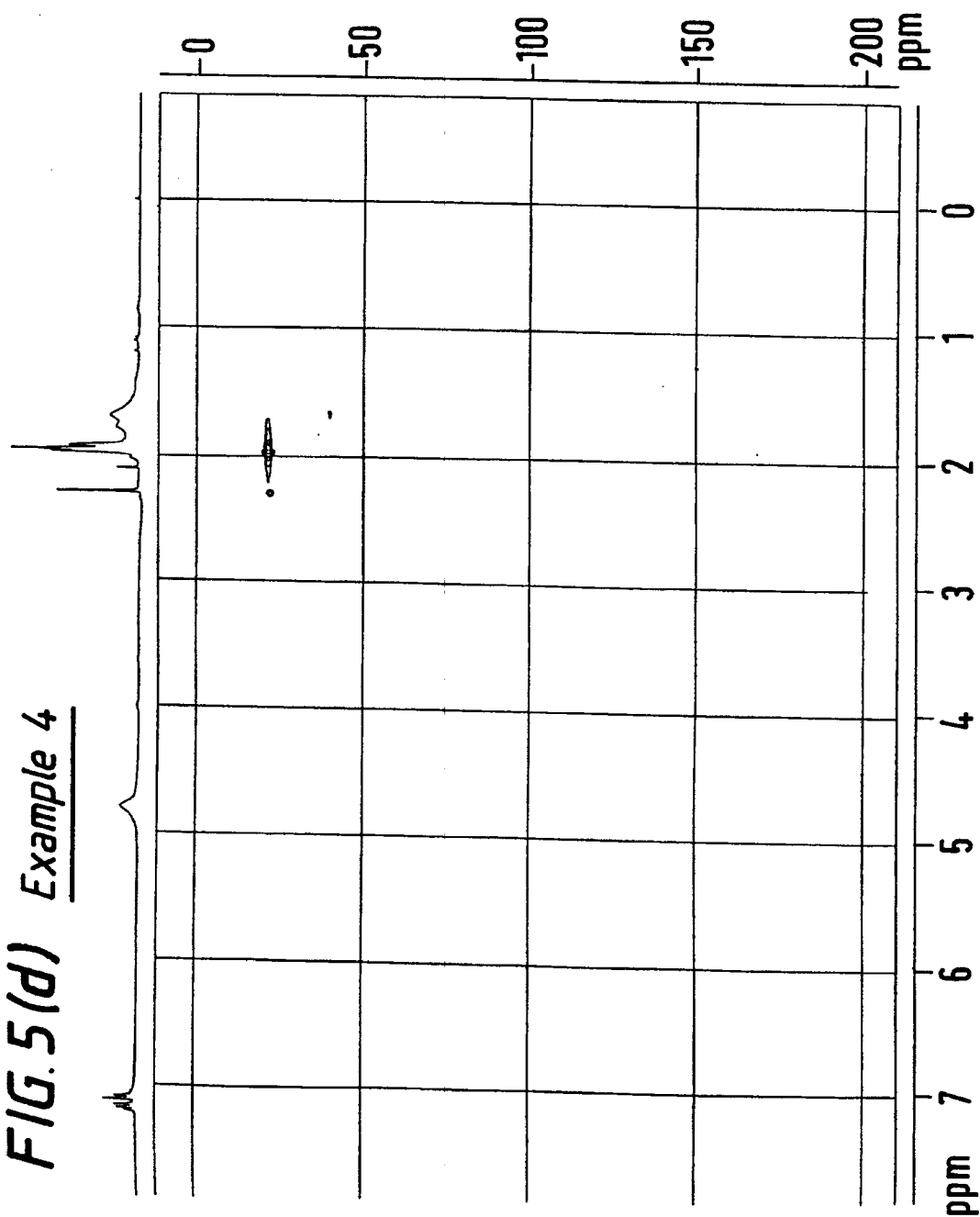
9/34



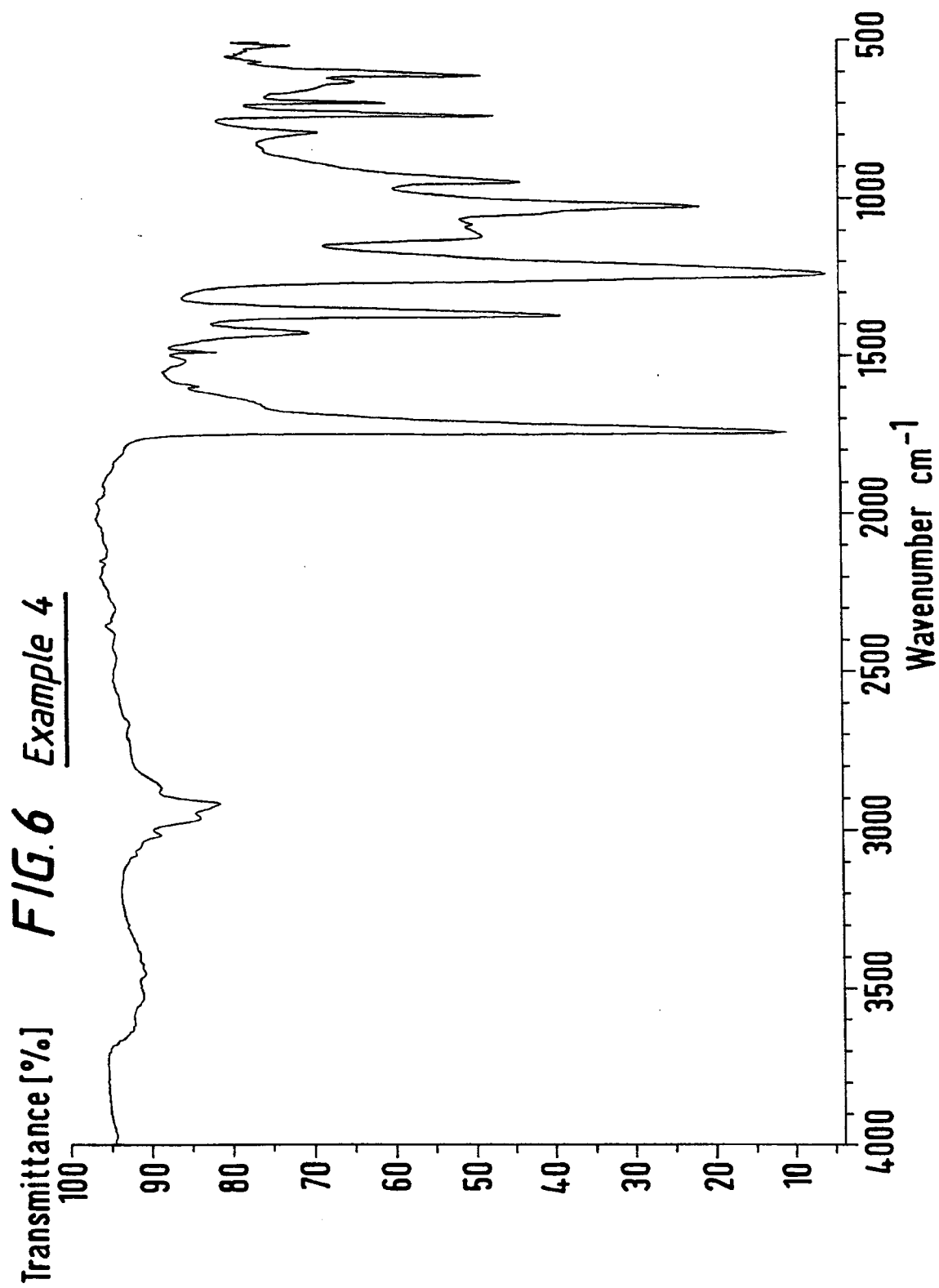
10/34

FIG. 5(c) Example 4

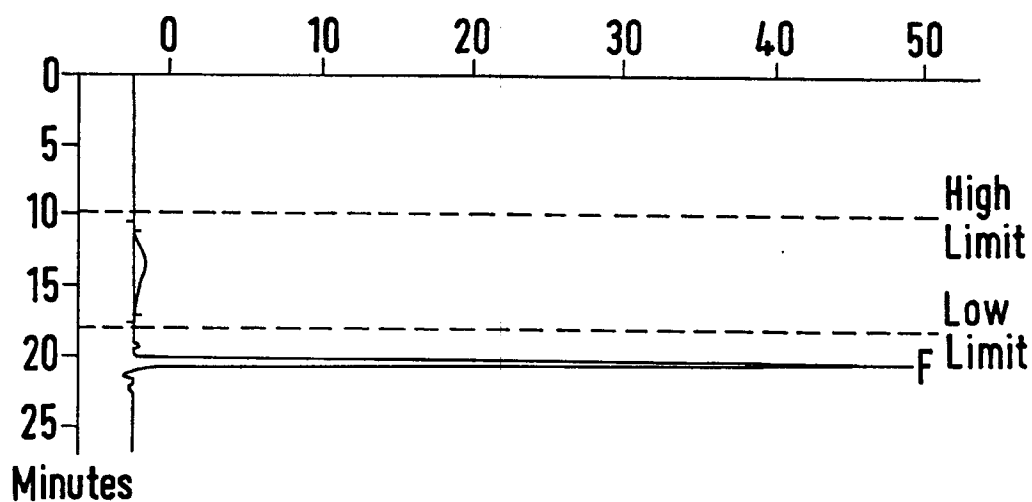
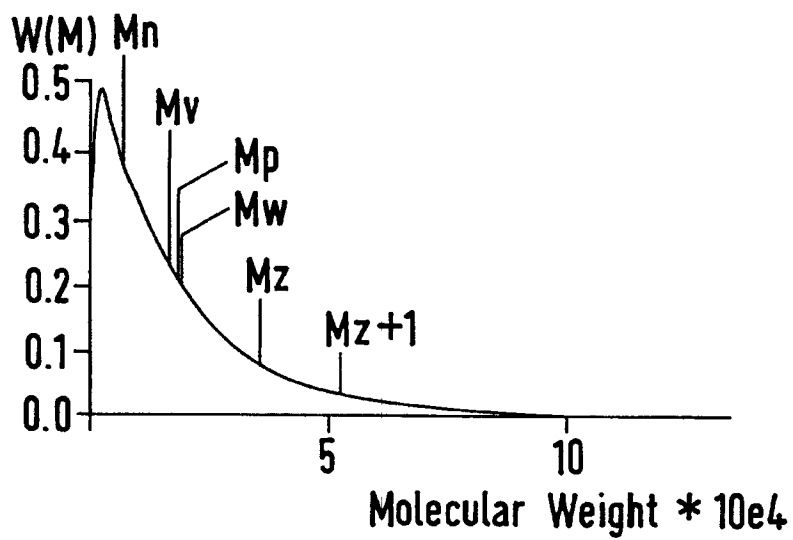
11/34

FIG. 5(d) Example 4

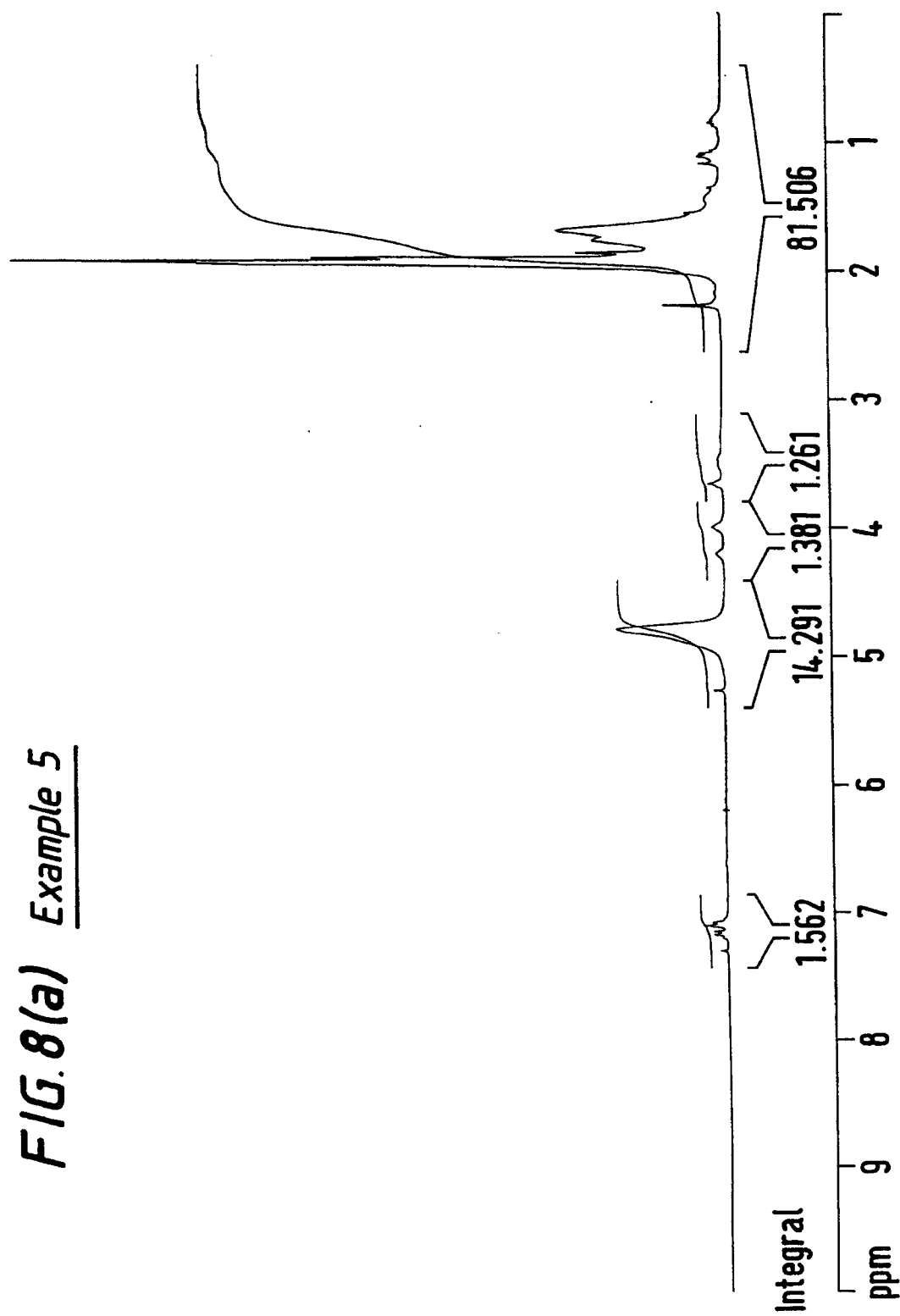
12/34



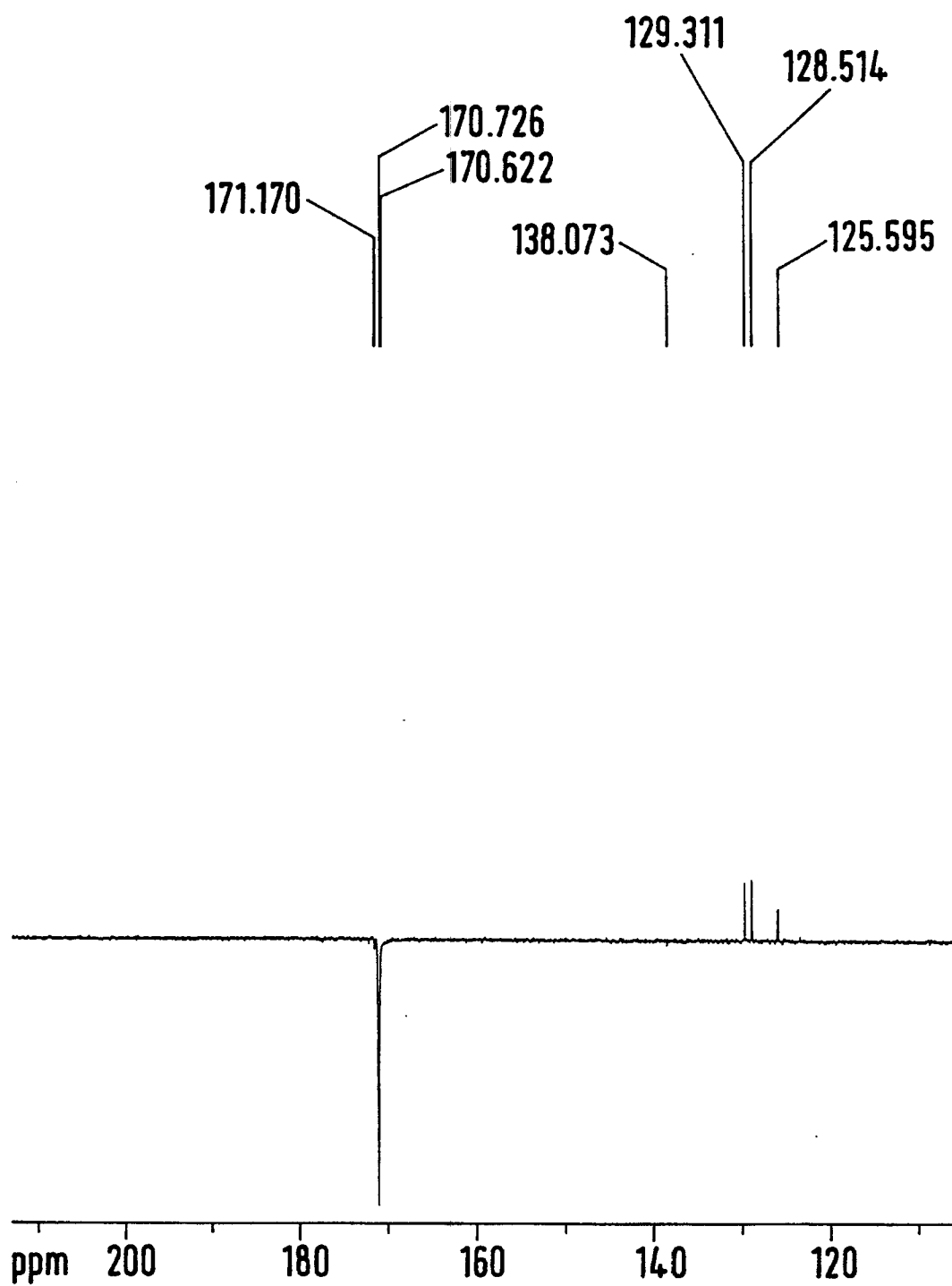
13/34

FIG.7 Example 4*Raw Chromatogram:**W(M) plot:*

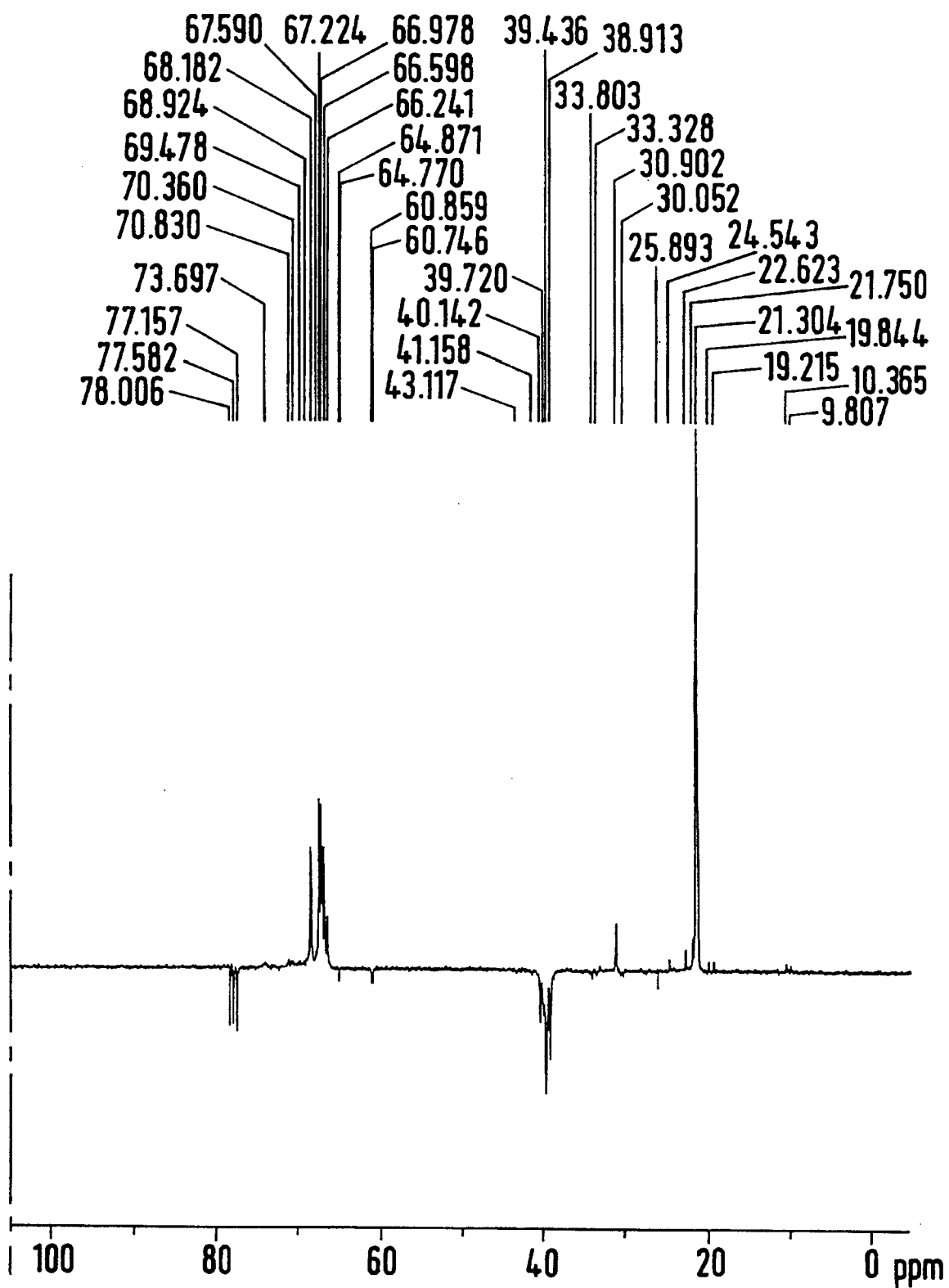
14/34

FIG. 8(a) Example 5

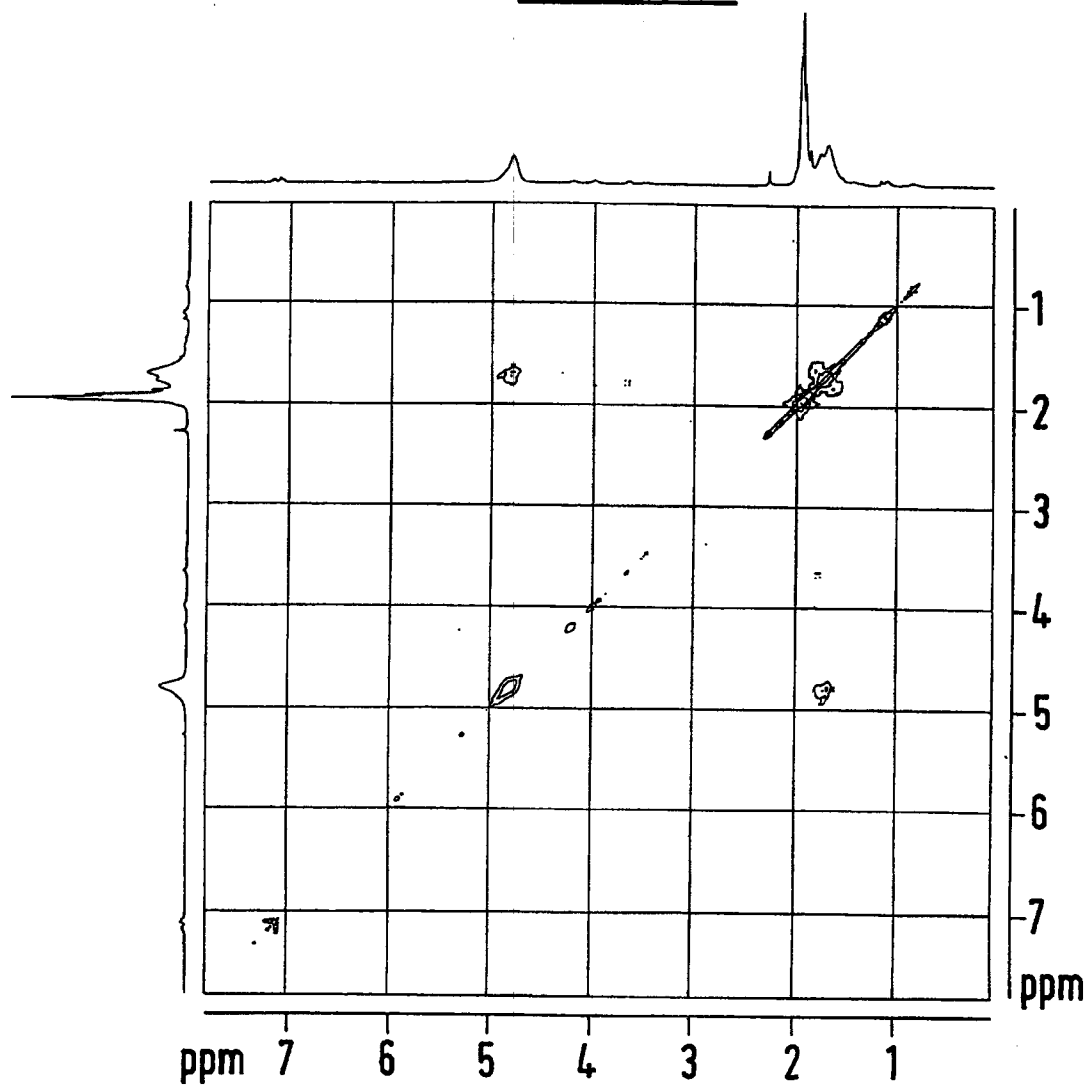
15/34
FIG. 8(b') Example 5



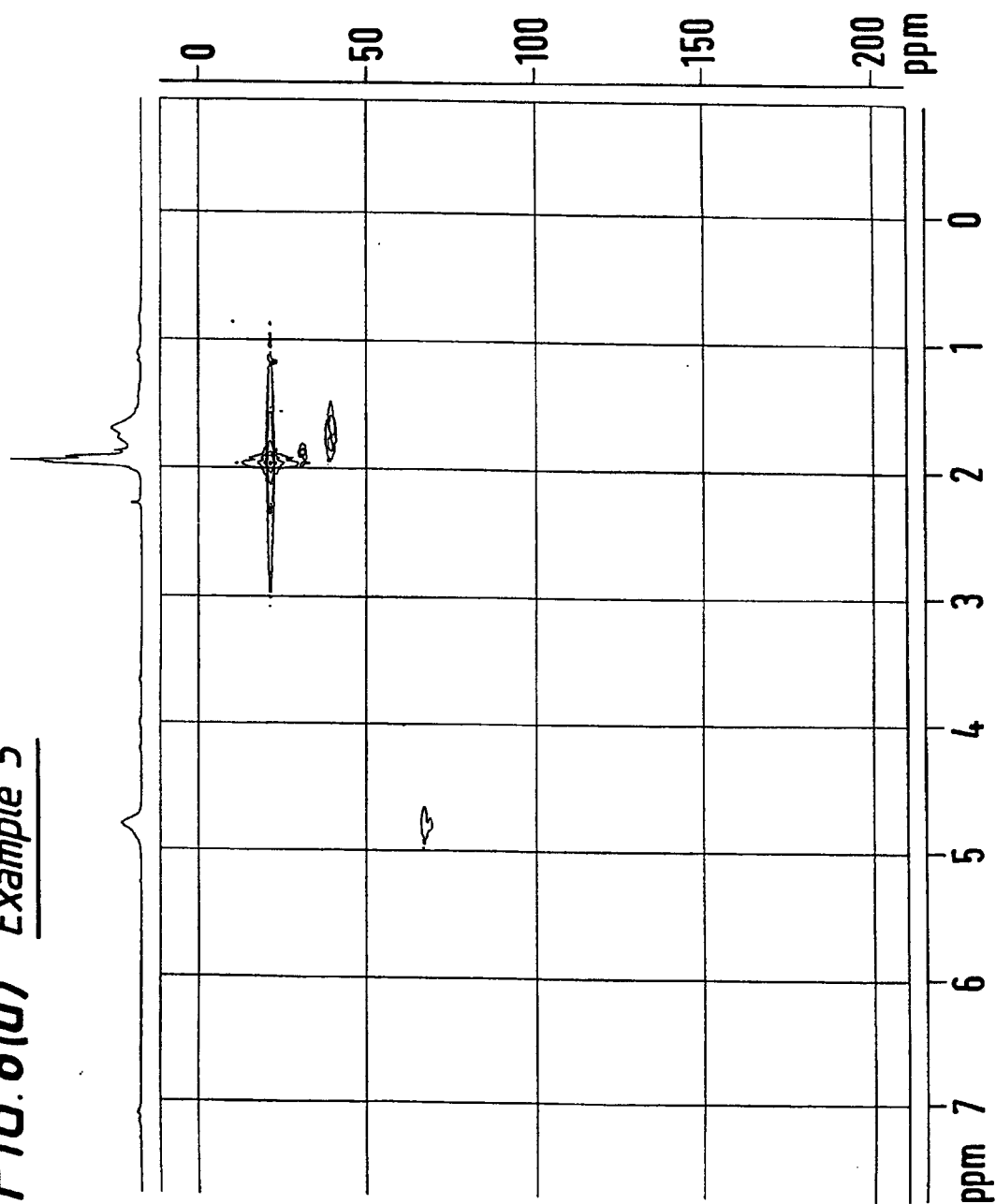
16/34

FIG. 8(b'') Example 5

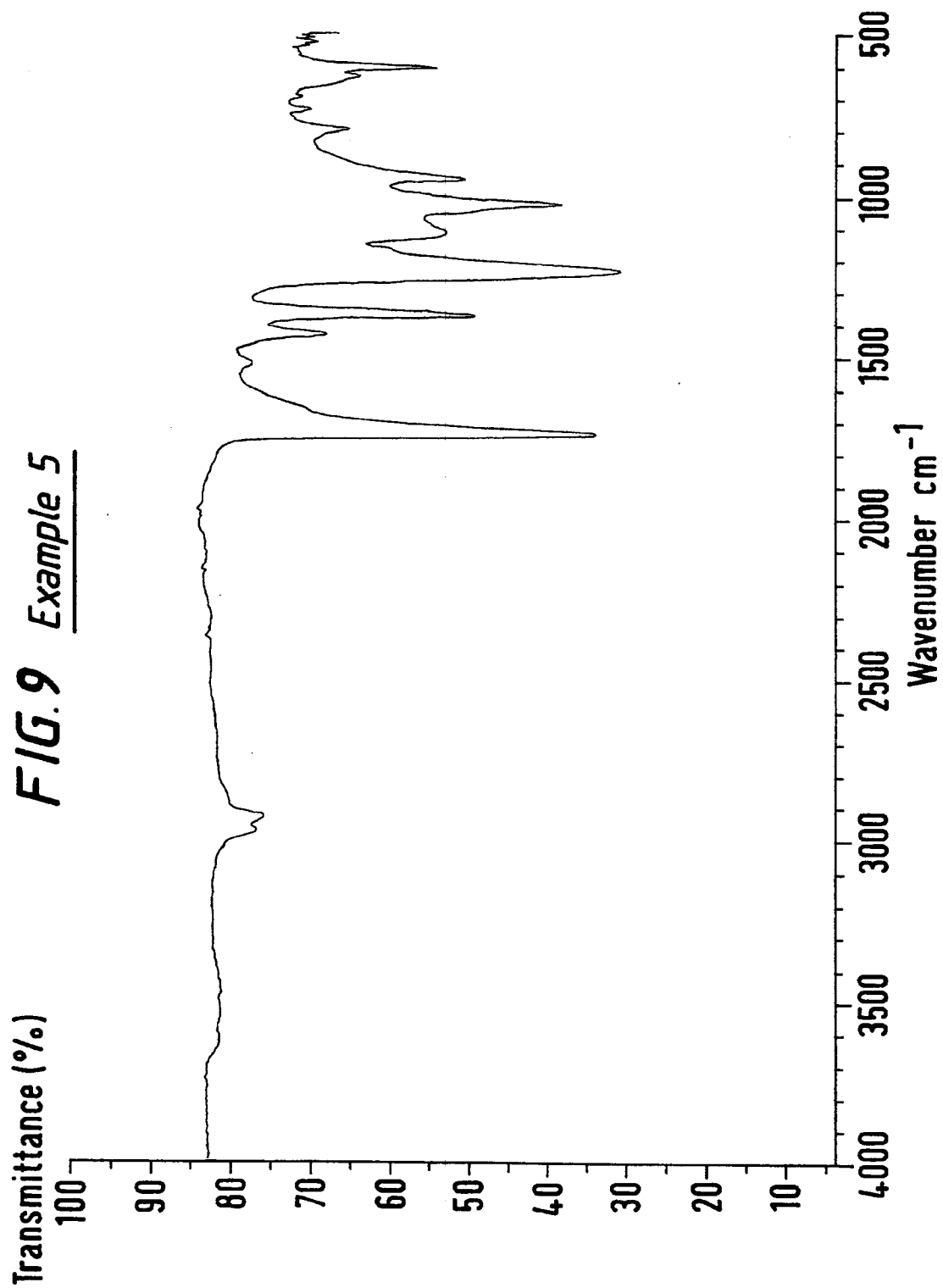
17/34

FIG. 8(c) Example 5

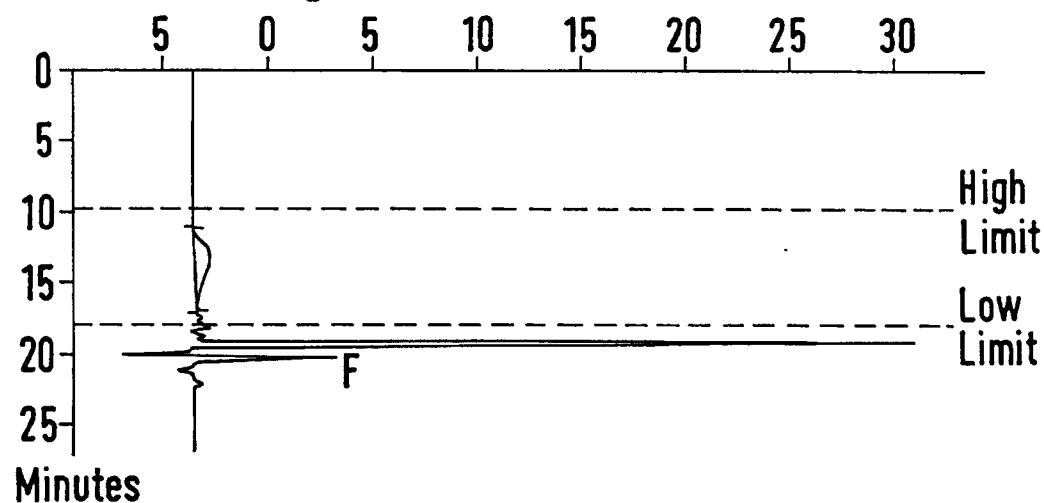
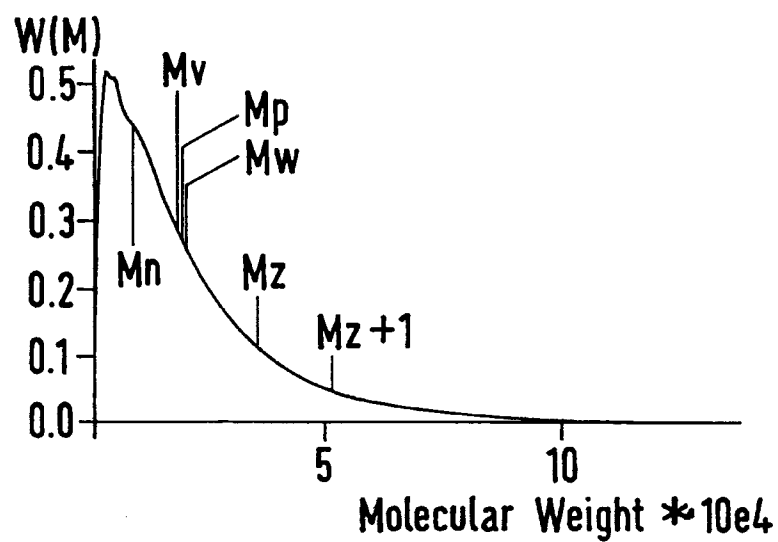
18/34

FIG. 8(d) Example 5

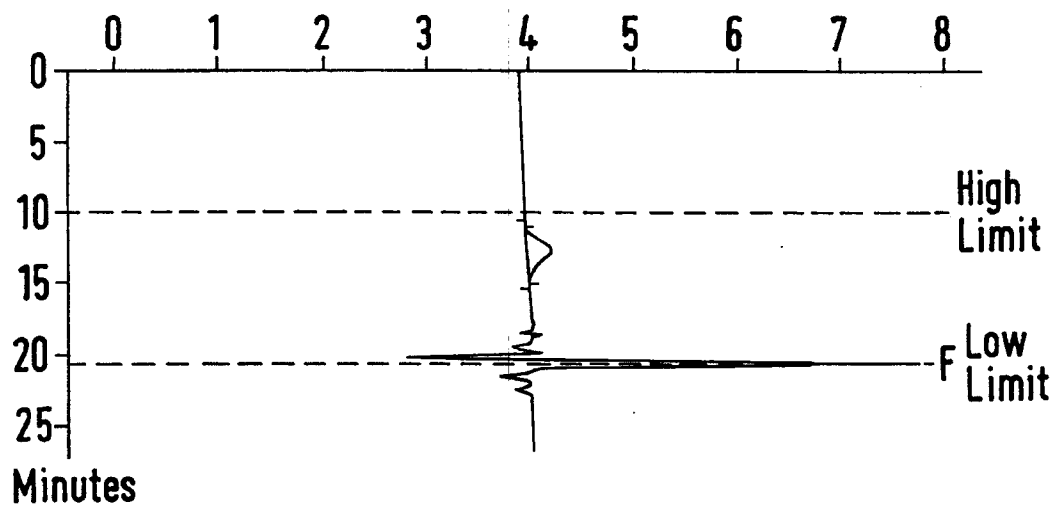
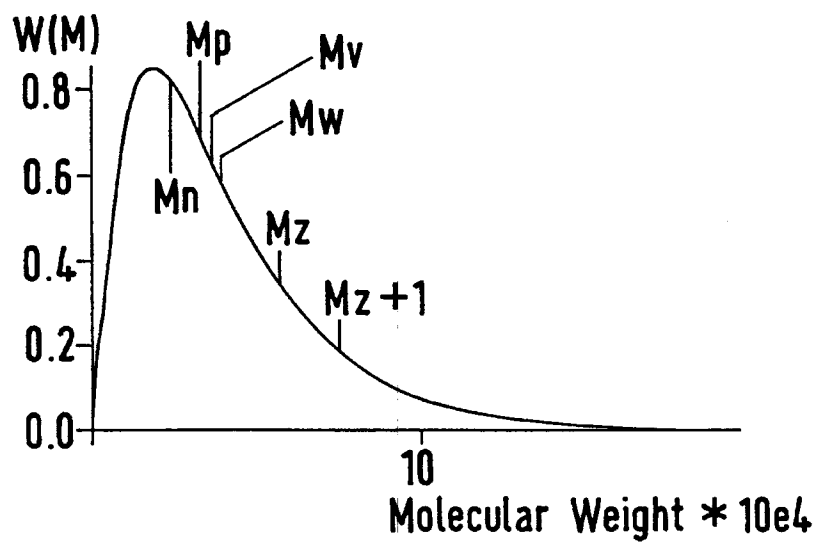
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FIG. 9 Example 5

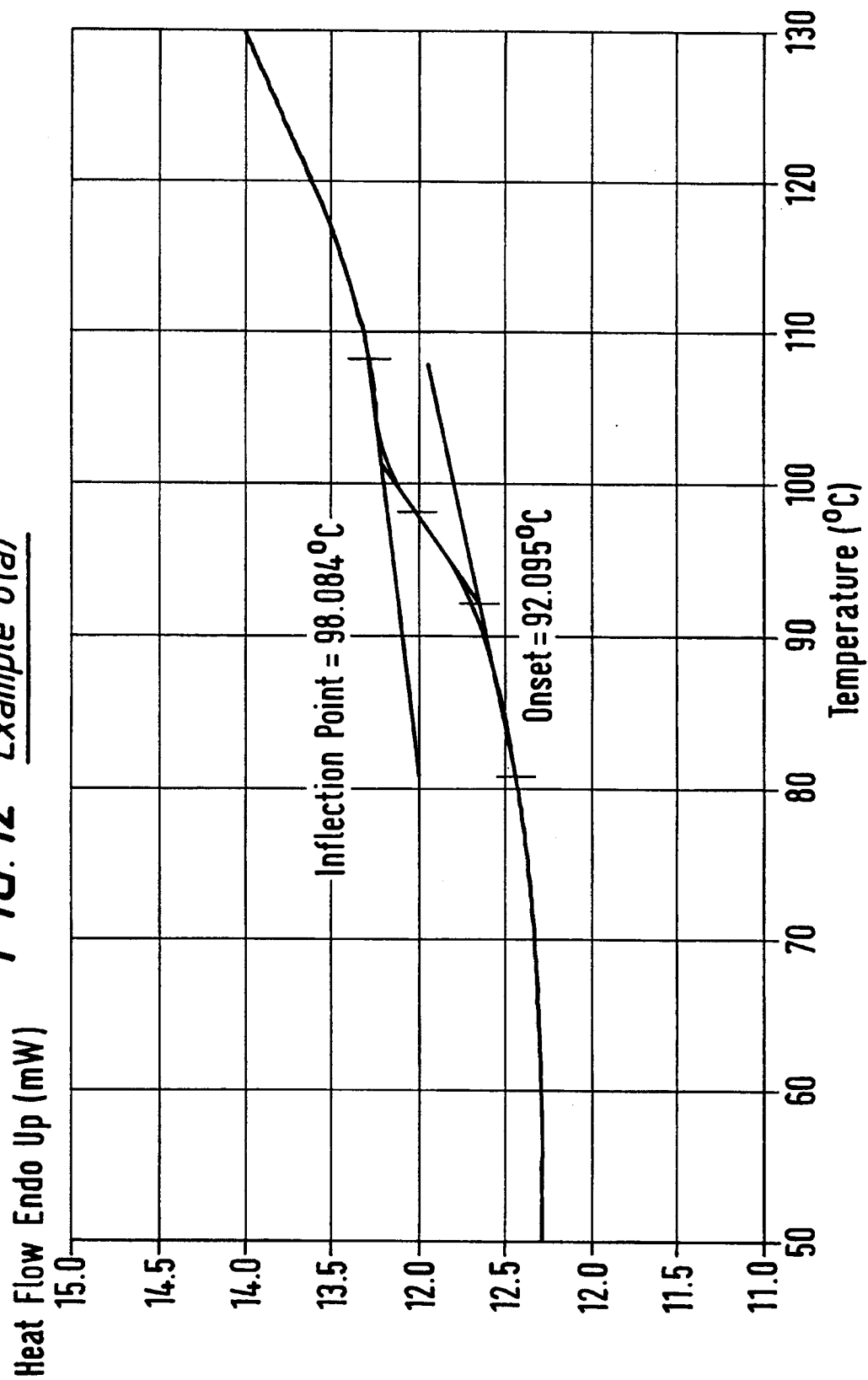
20/34

FIG. 10 Example 5*Raw Chromatogram:**W(M) plot:*

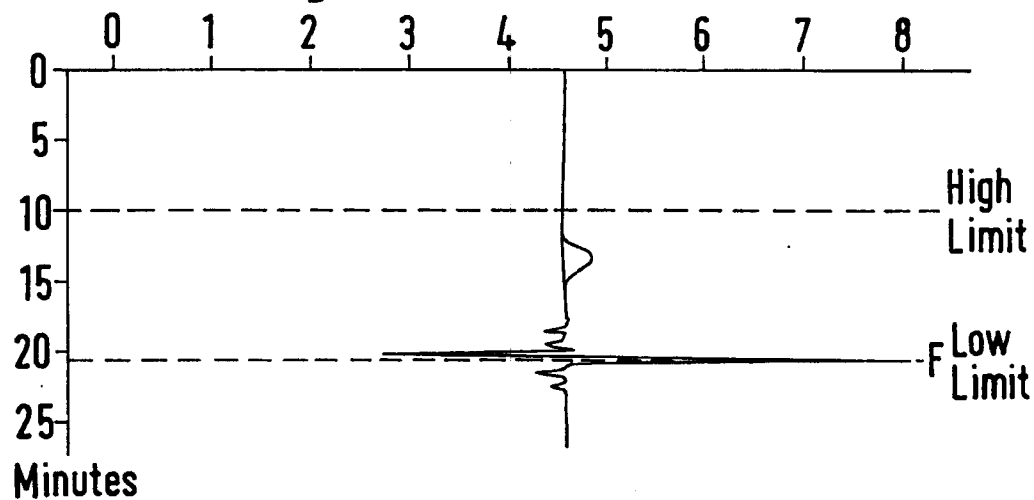
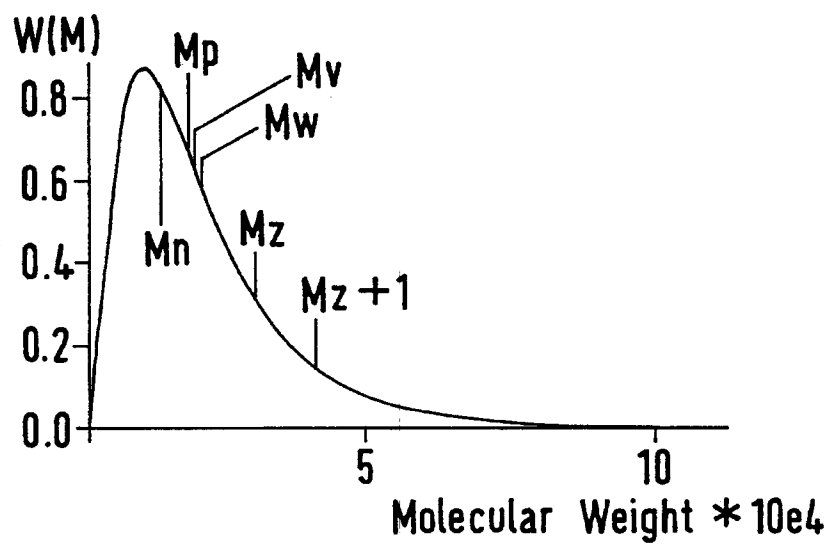
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FIG. 11 Example 6(a)*Raw Chromatogram:**W(M) plot:*

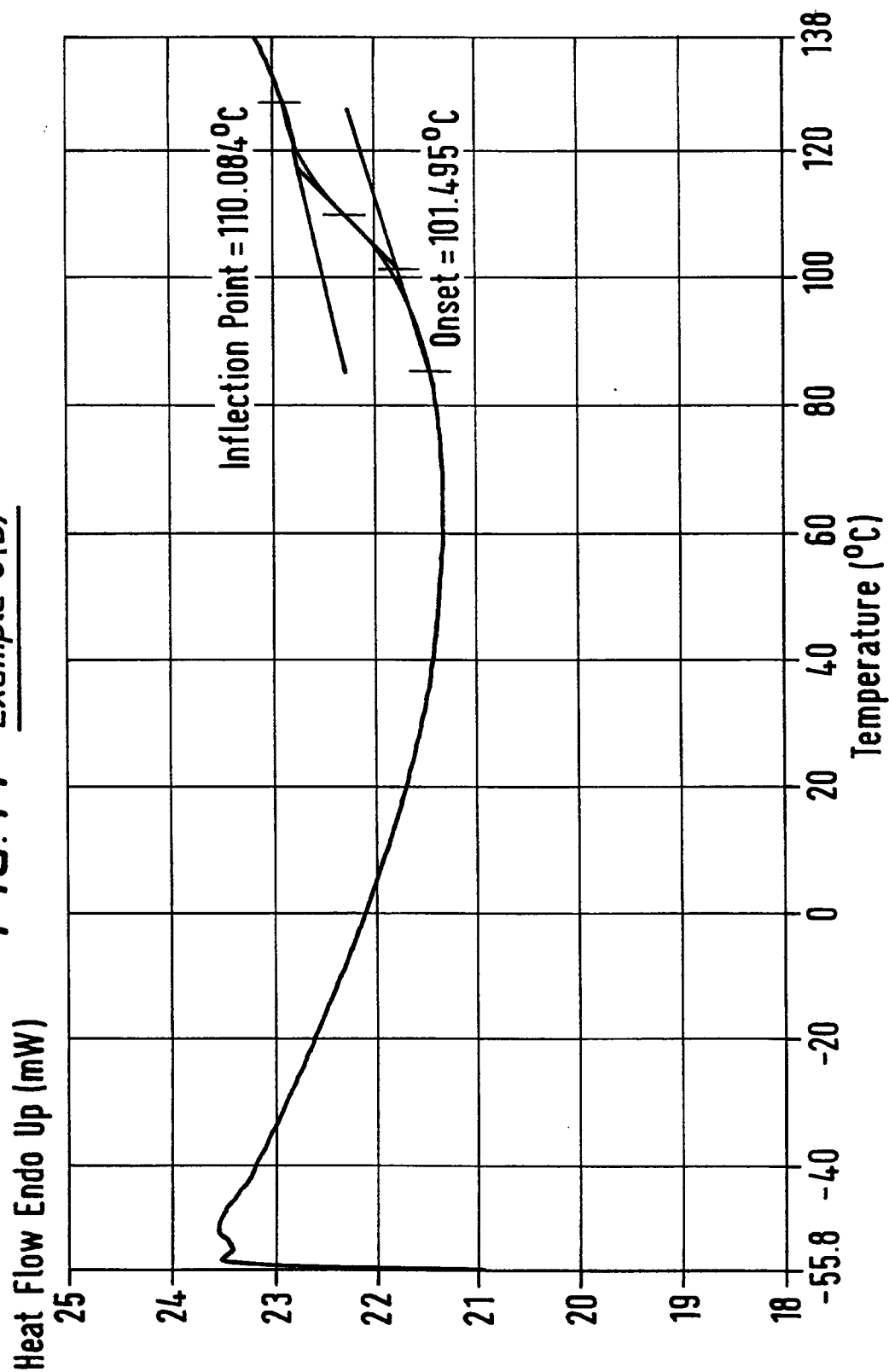
22/34

FIG. 12 Example 6(a)

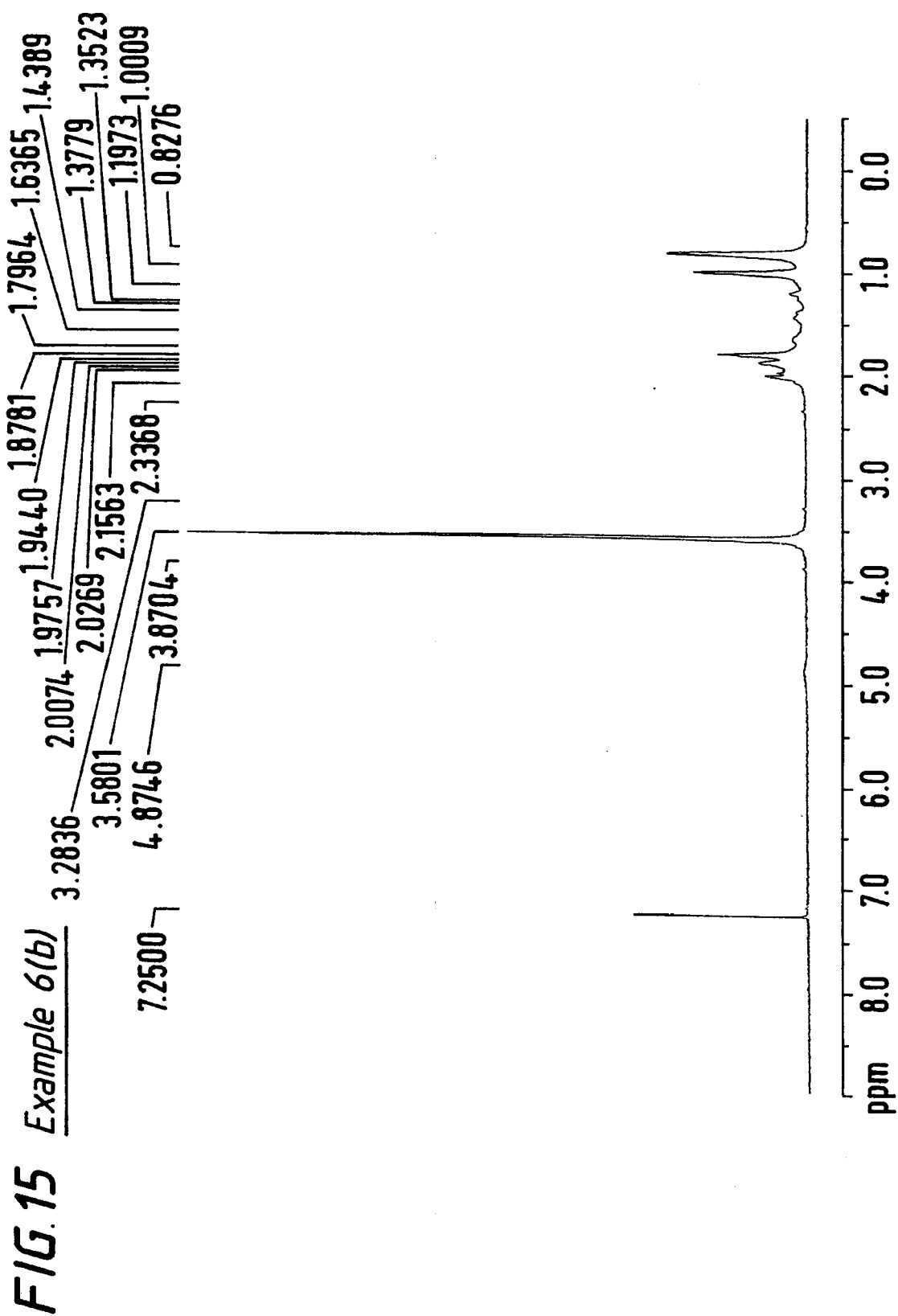
23/34

FIG. 13 Example 6(b)*Raw Chromatogram:**W(M) plot:*

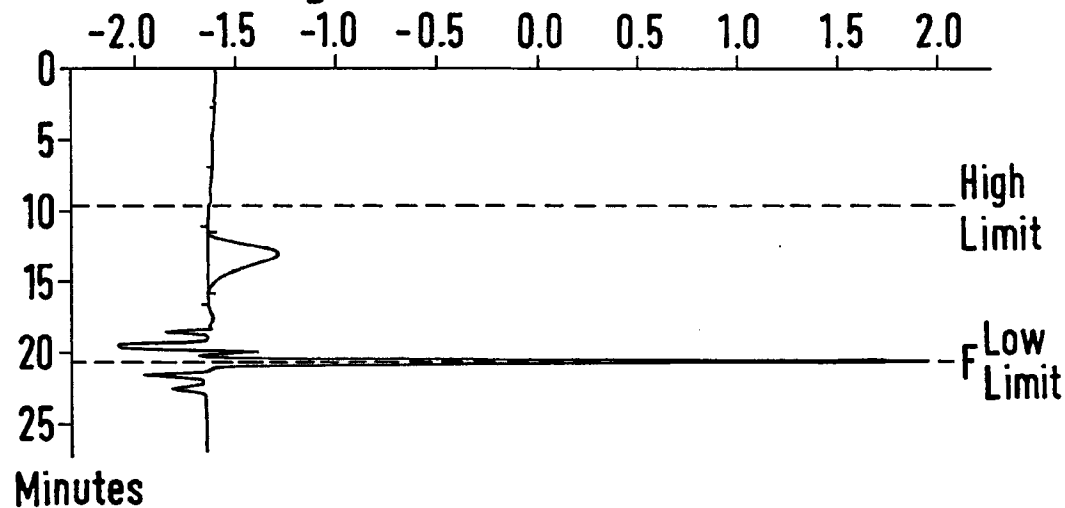
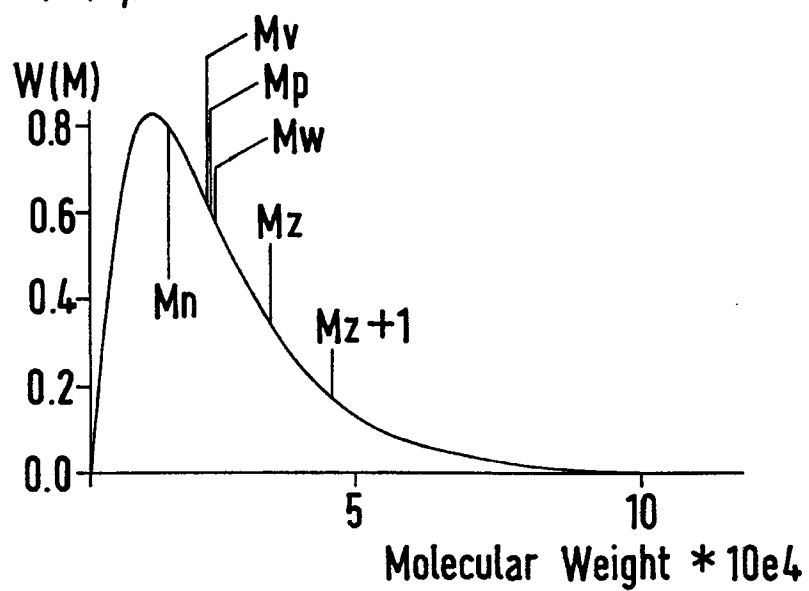
24/34

FIG. 14 Example 6(b)

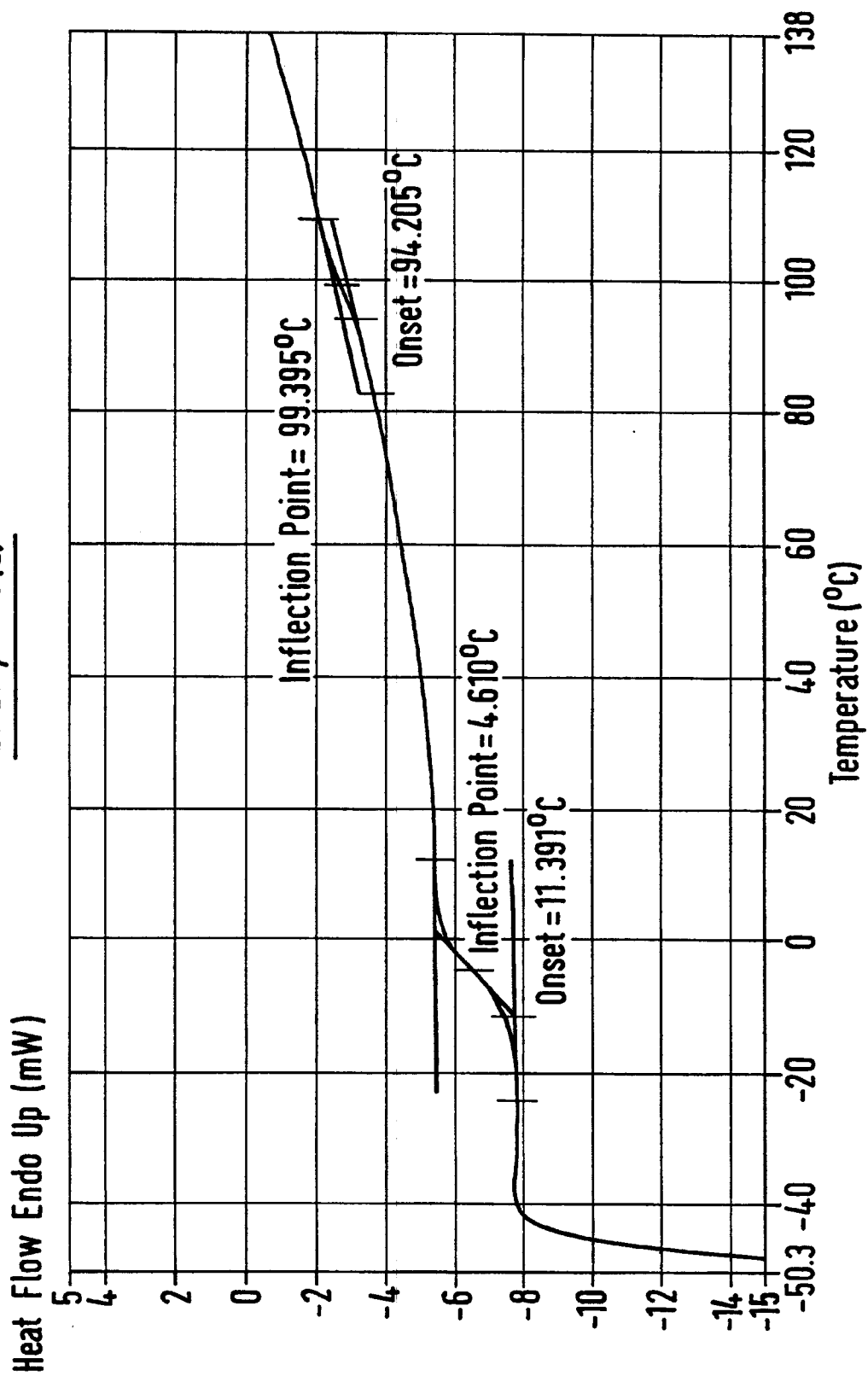
25/34



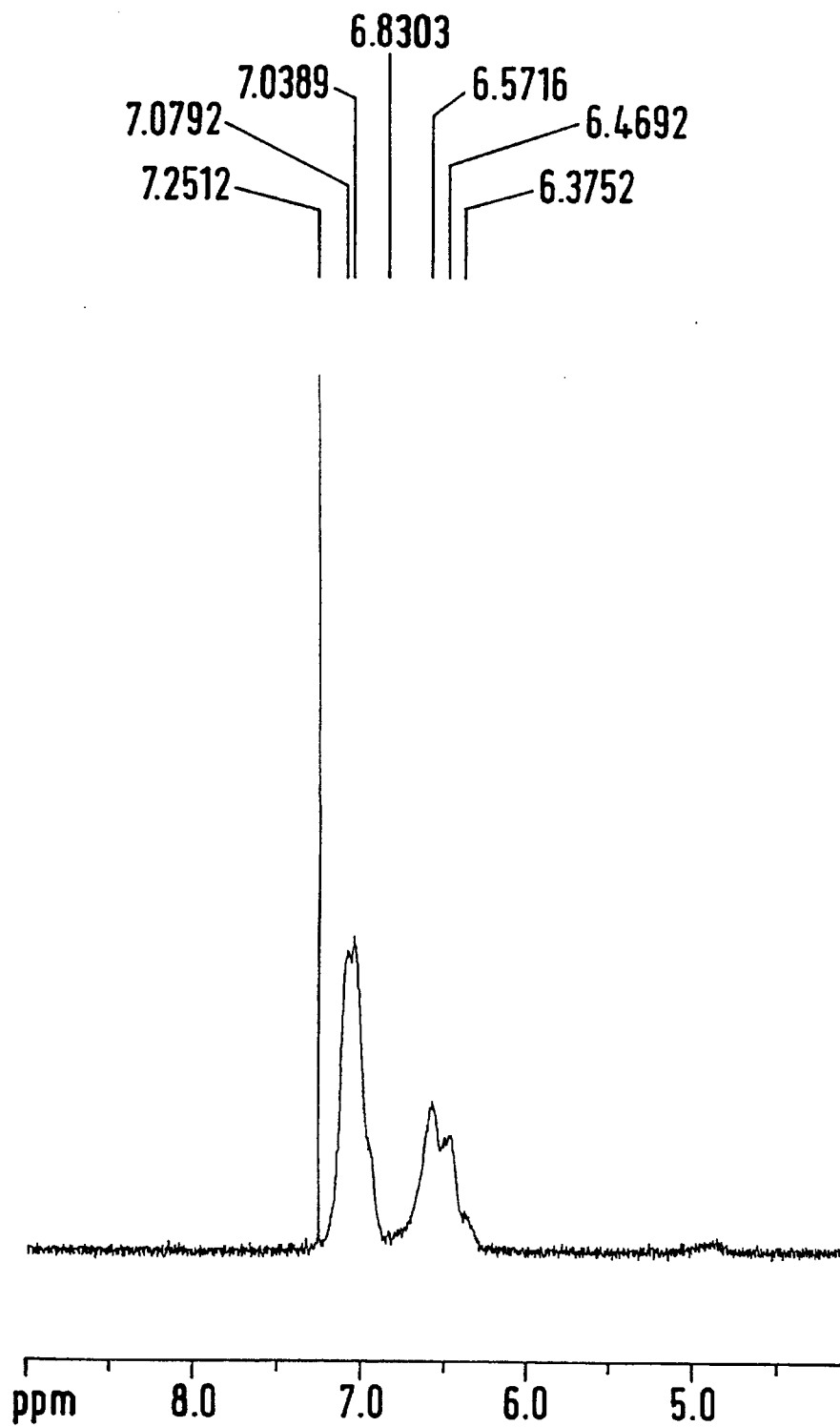
26/34

FIG. 16 Example 6(c)*Raw Chromatogram:**W(M) plot:*

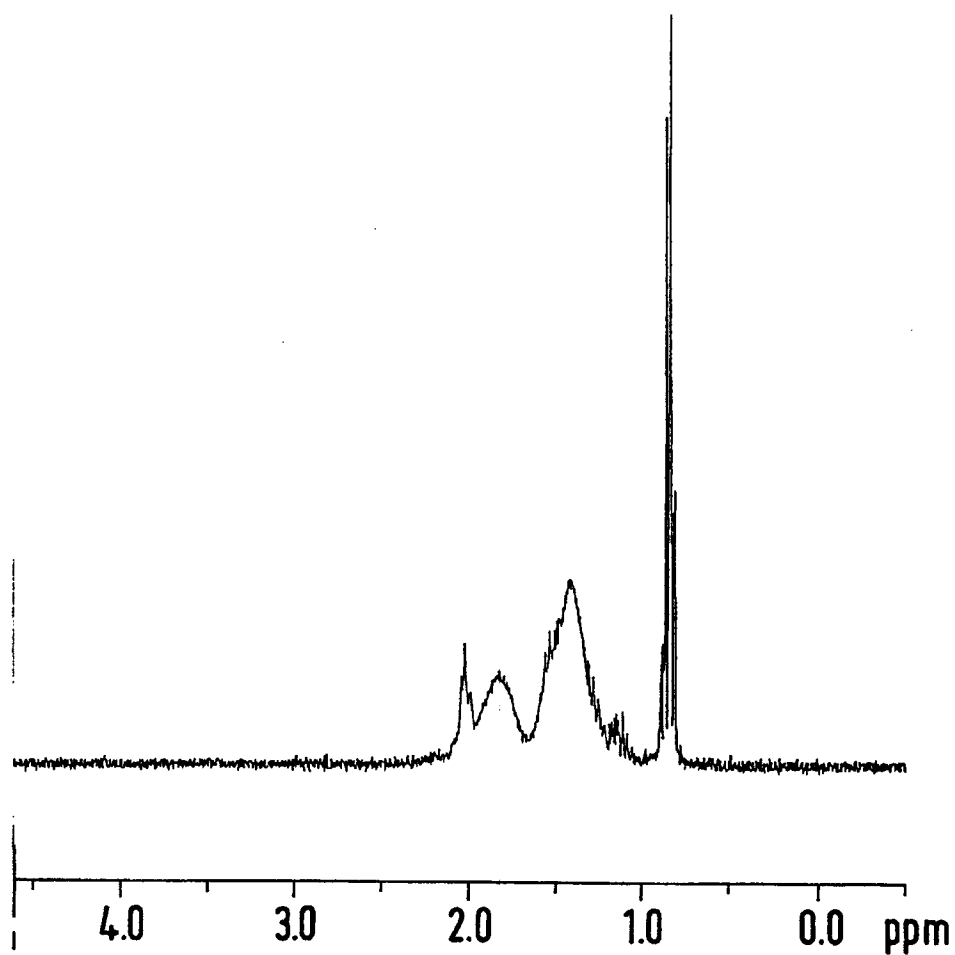
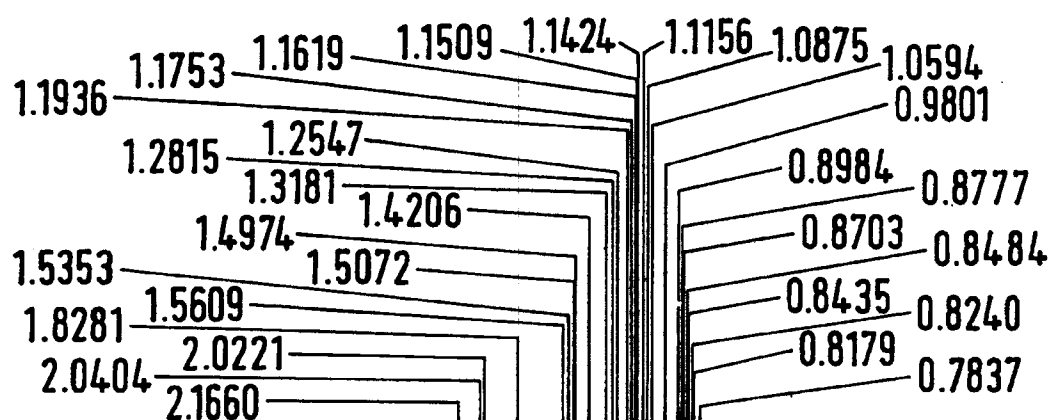
27/34

FIG. 17 Example 6(c)

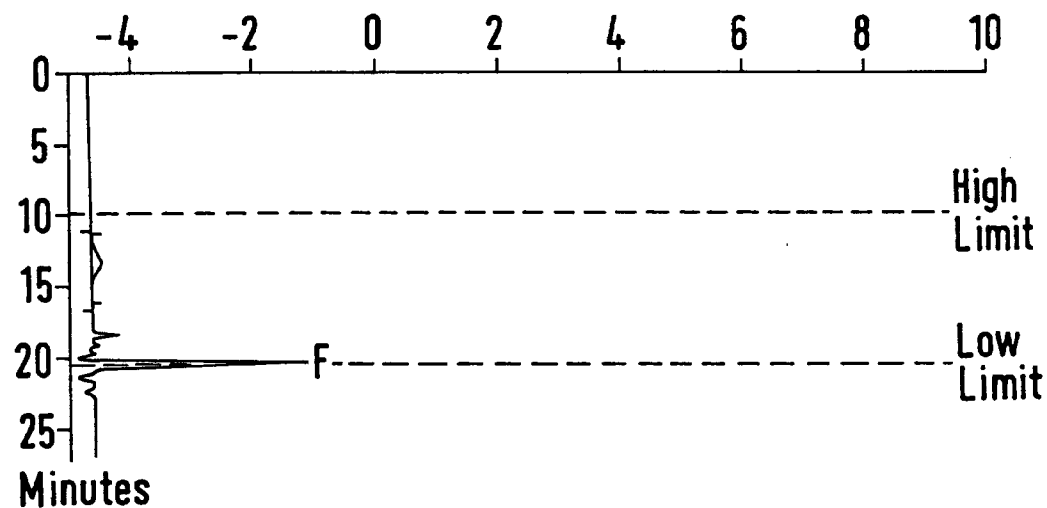
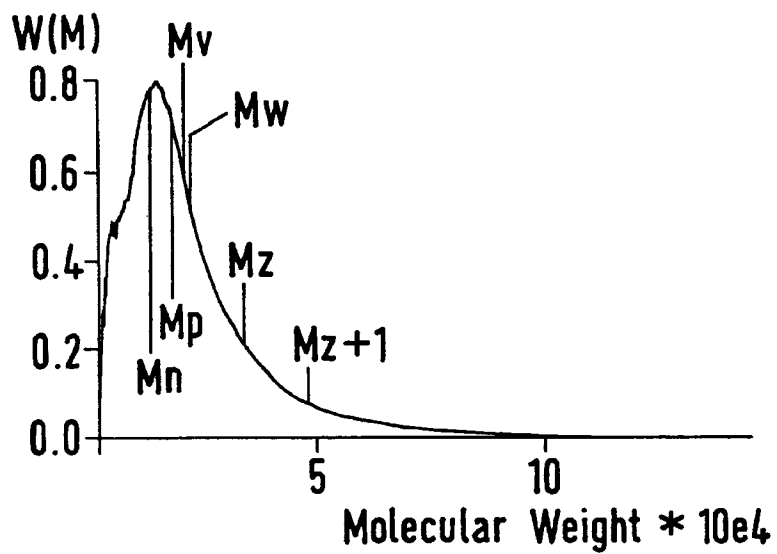
28/34

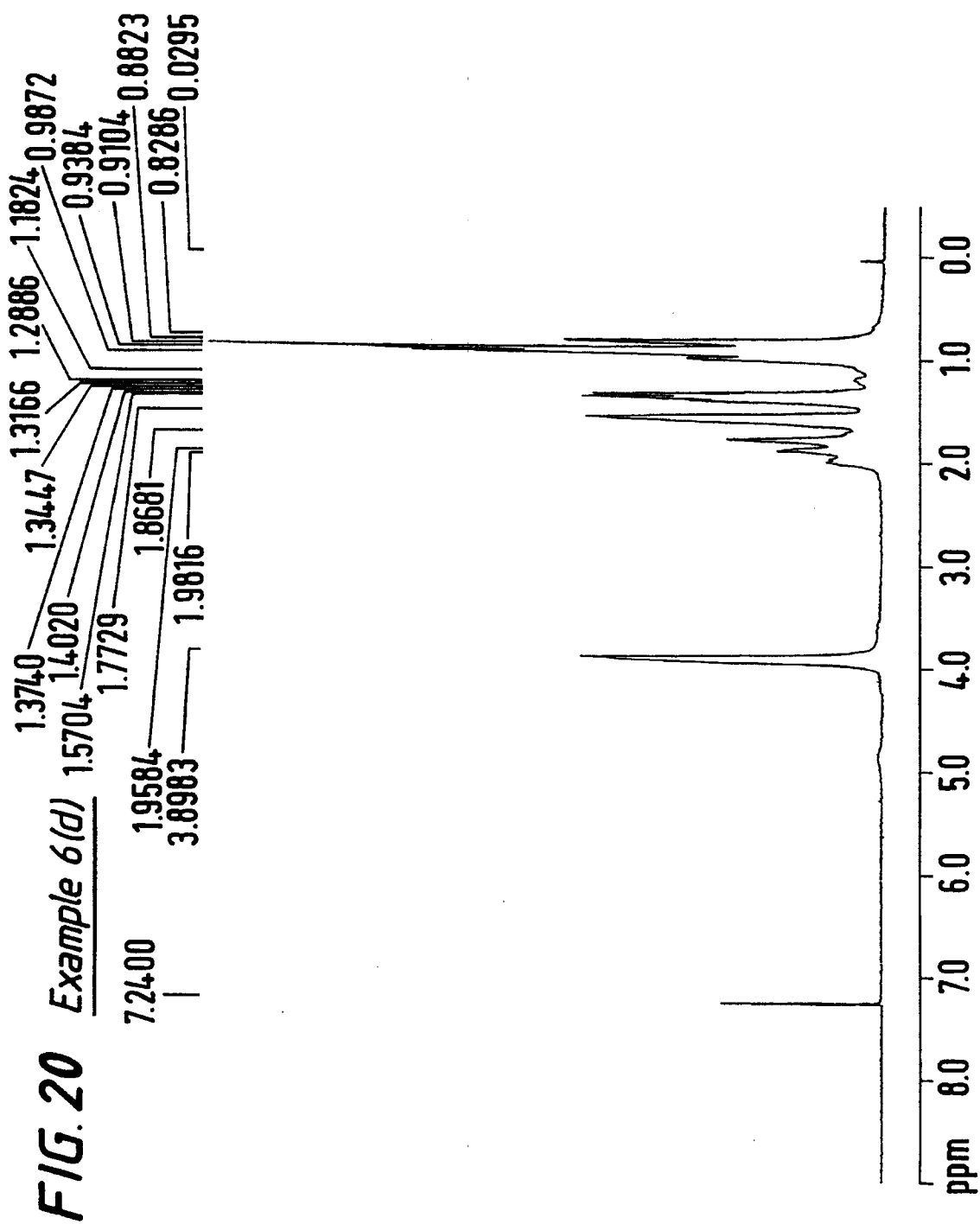
FIG. 18' Example 6(c)

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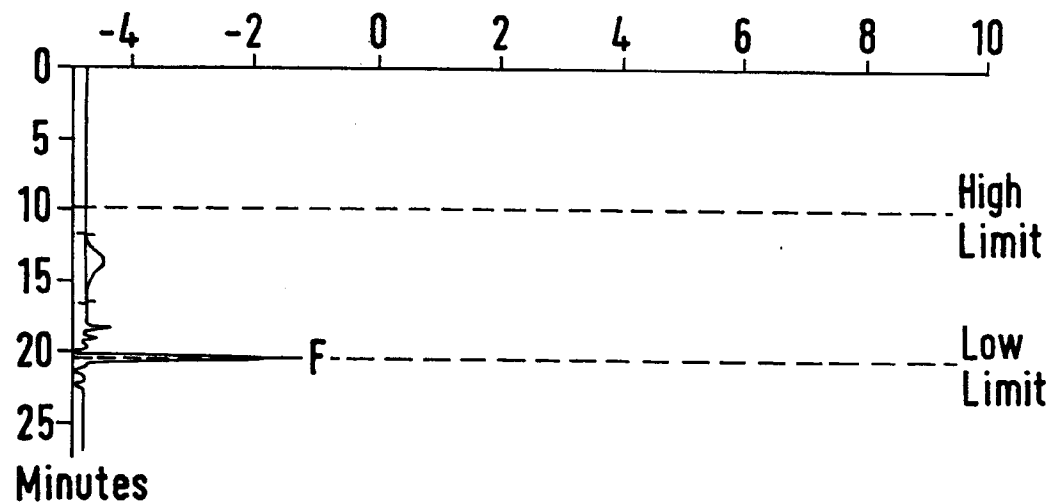
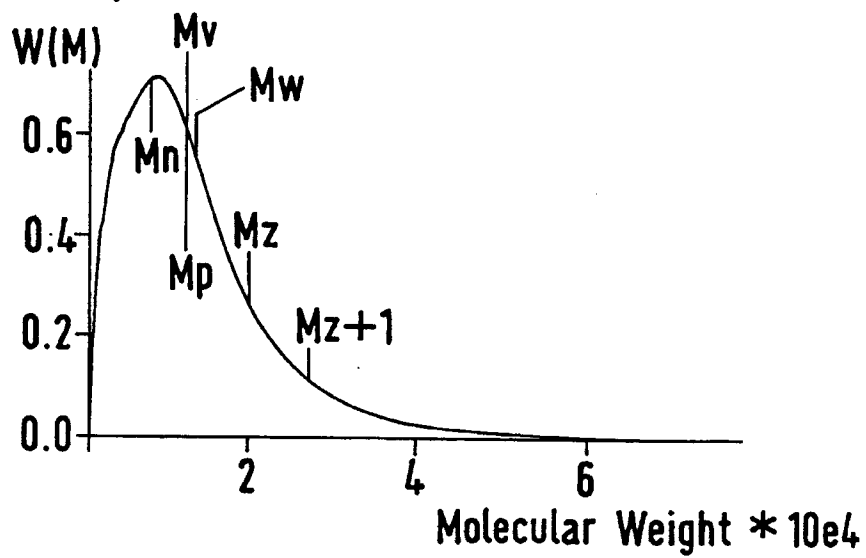
FIG. 18^{II} Example 6(c)

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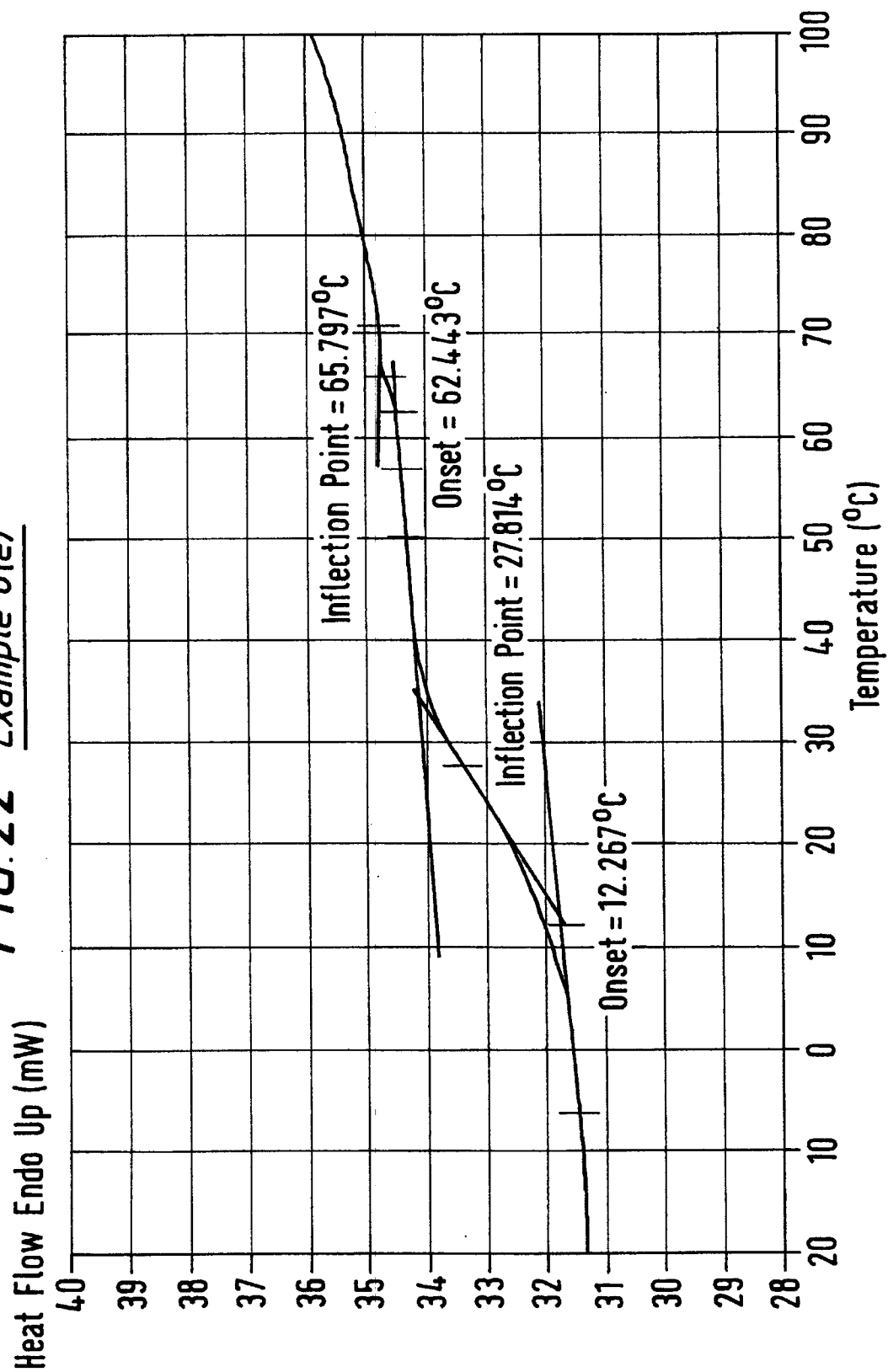
FIG. 19 Example 6(d)*Raw Chromatogram:**W(M) plot:*



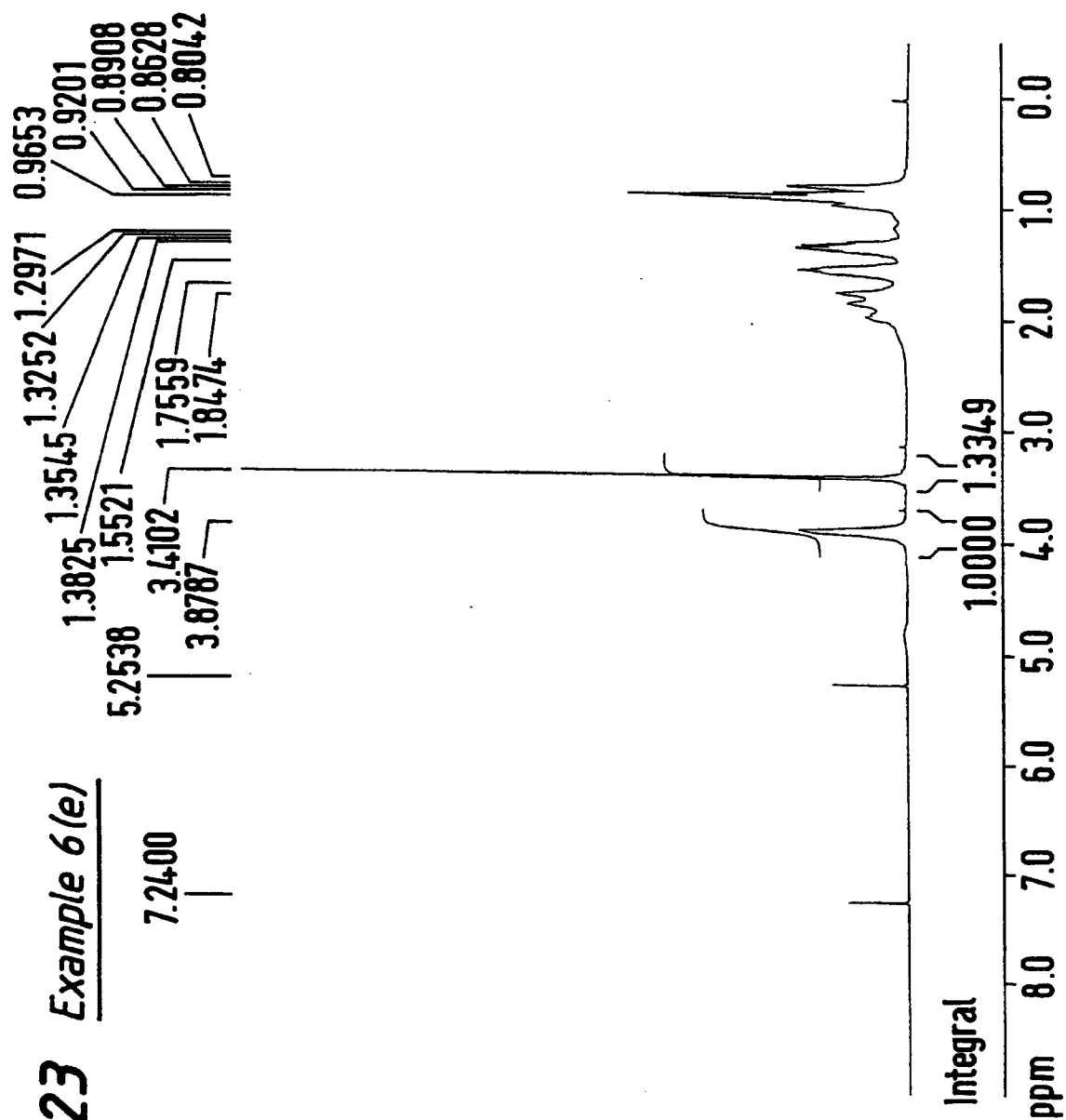
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FIG. 21 Example 6(e)**Raw Chromatogram:*****W(M) plot:***

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FIG. 22 Example 6(e)

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FIG. 23 Example 6(e)



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(21) International Application Number: PCT/IB98/00784 (22) International Filing Date: 20 May 1998 (20.05.98) (30) Priority Data: 08/864,255 28 May 1997 (28.05.97) US 08/940,101 29 September 1997 (29.09.97) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: BOLICH, Raymond, Edward, Jr.; 7201 Striker Road, Maineville, OH 45039 (US). JIVIDEN, Kathleen, Bridget; 2653 Timber Court, Lebanon, OH 45036 (US). MIDHA, Sanjeev; Apartment 2D, 9274 Deercross Parkway, Blue Ash, OH 45236 (US). MORRISSEY, Christopher, Todd; 8736 Charleston Woods Drive, Mason, OH 45040 (US). TORGERSON, Peter, Marte; 4127 U.S. Route 35 N.W., Washington Court House, OH 43160 (US). YANG, Jian, Zhong; 1-215-727, Koyo-cho Naka 2-chome, Higashinada-ku, Kobe 658 (JP). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS (57) Abstract <p>The present invention relates to hairspray compositions comprising from about 50 % to about 99.9 % by weight of an alcohol solvent, and from about 0.1 % to about 30 % by weight of a silicone-containing adhesive block copolymer having a weight average molecular weight from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with select silicone macroinitiators, preferably silicone macroazoinitiators. The hairspray compositions, when dried, preferably have a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, an impact strength of greater than about 7000 ergs, and an improved removeability from hair as defined by a hair stiffness value of from 0 to about 3.5 (0 to 4 scale) and a hair flaking value of from 0 to about 3.5 (0 to 4 scale). These hairspray compositions provide improved hair styling performance, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.</p>		

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HAIRSPRAY COMPOSITIONS CONTAINING SILICONE BLOCK COPOLYMERS

TECHNICAL FIELD

The present invention relates to hairspray compositions which provide improved hair style retention characteristics and hair feel. These compositions comprise a silicone-containing adhesive block polymer and at least about 50% by weight of an alcohol solvent.

BACKGROUND OF THE INVENTION

Hair styling compositions are well known and include compositions formulated for and intended for application as shampoos, hairsprays, aerosol mousses, and other formulations known for use in delivering hair styling polymers to the hair. These compositions are typically applied to wet or dry hair, depending on the formulation, and allowed to form thin hair styling films or welds to the applied surface.

Hair styling compositions are commonly formulated as hairsprays intended for application to dry, positioned or styled hair to maintain or hold the position of such dry, styled hair. These hairsprays are typically applied to the hair as pump sprays or from pressurized aerosol canisters. Such compositions provide temporary setting benefits to dry, styled hair and can usually be removed by water or by the next shampooing. The hair styling materials used in hairspray compositions are generally in the form of resins, gums, and adhesive polymers.

Many hairsprays, however, tend to deposit hair styling material on the hair that leaves the hair either excessively stiff or excessively sticky after the material has been applied to the hair and allowed to dry. Excessively stiff hairsprays are brittle and break down under common stresses such as wind, brushing, combing, and often feel or look unnatural. On the other extreme, excessively sticky hairsprays are more flexible under stress and are not excessively brittle, but leave the hair with a heavy, coated feel and a limp appearance as the hair droops and does not readily maintain or hold the intended style of the hair. These excessively sticky hairsprays also cause the hair to quickly become soiled from dust, dirt, lint, sebum, and other common contaminants that more readily adhere to the sticky hairsprays.

Some hairsprays have been formulated which can be applied to clean, dry hair to maintain or hold the desired hair style, and which are neither excessively stiff

or sticky after application. However, many of these hairsprays still cause the hair to droop excessively immediately after application to the dry, styled or positioned hair. The applied hairspray then solidifies on the hair, and then retains the drooped or otherwise limper position of the hair caused by the initial application of the hairspray.

It has now been found that the hairspray compositions of the present invention are especially effective in providing hair styling performance when applied to dry, styled or positioned hair, without causing the hair to be excessively stiff or sticky and without causing the hair to excessively droop immediately after application. These hairspray compositions comprise select silicone-containing adhesive copolymers in combination with an alcohol solvent, wherein the composition contains at least about 50% by weight of the alcohol solvent. The hairspray compositions when dried preferably have a cohesive strength of greater than about 0.5 kgf/mm^2 , a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm^3 , and an impact strength of greater than about 7000 ergs.

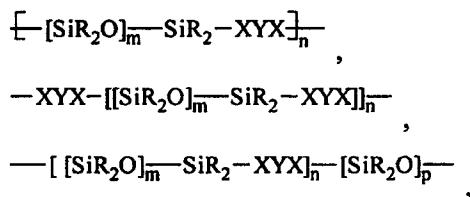
It has also been found that the preferred hair spray compositions of the present invention have an improved removeability from hair during shampooing, wherein the removeability is defined in terms of hair stiffness and hair flaking values ranging from 0 to about 3.5 (0 to 4 scale) These hair stiffness and flaking values are indirect measures of hair spray removeability. Each of these values are determined in accordance with the methodology defined herein.

It is therefore an object of the present invention to provide hairspray compositions that are neither excessively sticky nor excessively stiff after application, and further to provide such a composition that causes minimal or no drooping of dry, styled or positioned hair after application, and further to provide a hairspray composition having an improved removeability as defined herein. It is yet another object of the present invention to provide such a composition which comprises select silicone-containing block polymers in combination with high concentrations of an alcohol solvent, and further to provide a method of styling dry, styled or positioned hair without causing excessive drooping of the dry hair immediately after application and without causing the hair to feel excessively stiff or sticky.

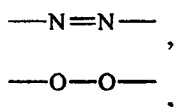
SUMMARY OF THE INVENTION

The present invention relates to hairspray compositions comprising from about 50% to about 99.9% by weight of an alcohol solvent, from about 0.1% to about 30% by weight of a silicone-containing adhesive block polymer having a

weight average molecular weight of from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with a silicone macroinitiator, wherein the silicone macroinitiator contains a chemical group selected from the group consisting of



and combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof; X is a divalent radical; Y is selected from the group consisting of



and combinations thereof; m, n, and p are positive integers each independently having a value of 1 or greater.; and wherein the silicone macroinitiator has a number average molecular weight from about 500 grams/mole to about 500,000 grams/mole, and wherein the hairspray composition, when dried, preferably has a cohesive strength of greater than about 0.5 kgf/mm², a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm³, and an impact strength of greater than about 7000 ergs. The hair spray compositions preferably have improved removeability, wherein improved removeability is defined by a hair stiffness value of from 0 to about 3.5 and a hair flaking value of from 0 to 3.5 (0 to 4 scale)

It has been found that these hairspray compositions are especially effective in providing hair styling performance when applied to dry, styled or positioned hair. In particular, these hairspray compositions can be applied to dry, styled or positioned hair without causing the hair to be excessively stiff or sticky after the hairspray has dried onto the hair, and without causing the dry, styled or positioned hair to excessively droop immediately after application of the hairspray composition and before the applied composition solidifies and sets onto the hair.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an overhead view of a dumbbell-shaped planar dried hairspray film sample useful for measuring the physical properties such as the cohesive strength and total energy absorption per unit volume as described herein.

Fig. 2 illustrates a cross-sectional view, showing the thickness of the dumbbell-shaped dried film illustrated in Fig. 1.

DETAILED DESCRIPTION OF THE INVENTION

The hairspray compositions of the present invention comprise select silicone-containing adhesive block polymers in combination with an alcohol solvent. Each of these essential components, as well as preferred or optional components, are described in detail hereinafter.

All percentages, parts and ratios are by weight of the total referenced composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified.

All molecular weights as used herein are weight average molecular weights expressed as grams/mole, unless otherwise specified.

The term "suitable for application to human hair" as used herein, means that the compositions or components thereof so described are suitable for use in contact with human hair and the scalp and skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The term "adhesive" as used herein refers to the silicone-containing block copolymers in the hairspray composition of the present invention that when applied as a solution or dispersion to a surface and dried, e.g., the hair fibers, the block copolymer forms films or welds onto the applied surface. Such a film or weld will have adhesive and cohesive strength, as is understood by those skilled in the art.

The term "kgf" as used herein is a unit of measure characterized as kilogram of force subjected to gravitational acceleration, i.e. 9.82 m/s^2 .

The hairspray compositions of the present invention can comprise, consist of, or consist essentially of the essential elements of the invention described herein, as well as any of the additional or optional ingredients, components, or other limitations described herein.

Alcohol solvent

The hairspray compositions of the present invention comprise an alcohol solvent that dissolves or disperses the silicone-containing block copolymer described in detail hereinafter. Concentrations of the alcohol solvent ranges from about 50%

to about 99.9%, preferably from about 50% to about 90%, more preferably from about 55% to about 80%, by weight of the hairspray compositions.

Alcohol solvents suitable for use in the hairspray compositions of the present invention are preferably ethanol, n-propanol, isopropanol, and combinations, wherein the selected silicone-containing adhesive block polymer is soluble in the selected alcohol solvent at a concentration of at least about 0.1 mg/mL, preferably at least about 0.5 mg/mL, and more preferably at least about 1 mg/mL, at about 22.7°C.

The hairspray composition may further comprise other additional solvents, including water, provided that the silicone-containing block copolymer remains dissolved or otherwise dispersed in the hairspray composition, and provided that such additional solvents are chemically and physically compatible with the ingredients of the composition and that it does not substantially and unduly impair product performance. The hairspray compositions may further comprise up to about 45% by weight of water, preferably less than about 40%.

It has been found that the alcohol solvent, at the above-described concentrations, when used in combination with the select silicone-containing adhesive block polymers is especially effective at providing improved hair styling performance to the hairspray composition of the present invention. This combination of select polymers and alcohol solvents is even more effective in minimizing or eliminating the undesirable drooping of dry, styled or positioned hair immediately after application to the hair.

Adhesive Block Copolymer

The hairspray composition of the present invention comprises select silicone-containing adhesive block copolymers as defined herein, which help provide the improved hair styling performance to the composition, and which are soluble or dispersible in the alcohol solvent of the hairspray composition. Concentrations of the block copolymers in the hairspray composition ranges from about 0.1% to about 30%, preferably from about 0.5% to about 20%, and more preferably from about 0.5% to about 10%, by weight of the composition.

The silicone-containing adhesive block copolymers selected for use in the hairspray compositions of the present invention are prepared by the free radical polymerization of select silicone containing macroinitiators (described in detail hereinafter) and ethylenically unsaturated monomers. The resulting block copolymers comprise sequentially arranged moieties or blocks which are further composed of smaller repeating units. The silicone-containing adhesive block

copolymers herein comprise silicone-containing blocks derived from silicone-containing macroinitiators (hereinafter Block A) and other blocks derived from ethylenically unsaturated monomers as defined herein (hereinafter Block B). These block copolymers are either A-B block structures containing two block segments; A-B-A block structures containing three block segments, $-(A-B)_n-$ block structures containing multiple blocks wherein n is an integer having a value of 2 or more, or combinations thereof.

The hairspray compositions of the present invention comprises any one of the of the block structures described above, including mixtures or combinations thereof, and also including combinations thereof with small amounts of unreacted monomer or small amounts of homopolymers derived from the ethylenically unsaturated monomers described herein or the silicone-containing macroinitiators also described herein.

The silicone-containing adhesive block copolymers herein have a weight average molecular weight of from about 10,000 grams/mole to about 10,000,000 grams/mole, preferably from about 20,000 grams/mole to about 1,000,000 grams/mole, more preferably from about 30,000 grams/mole to about 1,000,000 grams/mole, even more preferably from about 60,000 grams/mole to about 750,000 grams/mole, and most preferably from about 70,000 grams/mole and about 750,000 grams/mole.

The silicone-containing adhesive block copolymers for use in the hairspray compositions herein are prepared by free radical polymerization of ethylenically unsaturated monomers and the silicone-containing macroinitiators described herein. Polymerization reactions of this type are generally well known in the polymer art, some descriptions of which are disclosed by M. Mishra, *Macromolecular Design: Concept and Practice*, Polymer Frontiers International, Inc., pages 313-358 (1994); European Patent Application 766957A1, published April 9, 1997; and Odian, *Principles of Polymerization*, 3rd edition, John Wiley & Sons, pages 198-334 (1991), which descriptions are incorporated herein by reference in their entirety.

The free radical polymerization reaction referenced herein can be accomplished, for example, by combining the ethylenically unsaturated monomer and the polysiloxane macroinitiator in a reactor along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This can be done by evacuation or by purging with an inert gas, such as argon or nitrogen. The reaction is brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can

be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The resulting block copolymer can be further purified, as desired, and used in formulating the hairspray composition of the present invention by formulation techniques well known in the art.

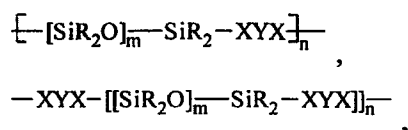
The silicone-containing adhesive block copolymers for use herein can also be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers or macromonomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

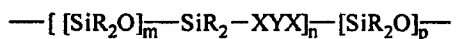
Other examples of silicone-containing block copolymers and methods of making them are described in U.S. Patent 5,523,365, to Geck et al., issued June 4, 1996; U.S. Patent 4,689,289, to Crivello, issued August 25, 1987; U.S. Patent 4,584,356, to Crivello, issued April 22, 1986; Macromolecular Design, Concept & Practice, Ed: M.K. Mishra, Polymer Frontiers International, Inc., Hopewell Jct., NY (1994); and Block Copolymers, A. Noshay and J.E. McGrath, Academic Press, NY (1977), which descriptions are incorporated herein by reference.

Silicone-containing Macroinitiator

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of silicone-containing blocks, wherein the silicone-containing blocks are derived from the select silicone-containing macroinitiators described herein.

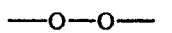
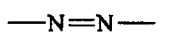
The silicone-containing macroinitiator for use in the hairspray composition of the present invention is selected from the group consisting of the following formulas:





or combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof, preferably methyl group; each X is a divalent linking group which may be the same or different for any given silicone-containing macroazoinitiator, and which may include the following groups: acyl, alkyl, aryl, amide, alkene, alkyne, ether, ester, sulfone, sulfoxide, thioether, halogen, nitrile and combinations thereof, preferably amide or ester groups for ease of synthesis. Other divalent linking groups can also be used provided that they do not substantially and unduly impair the free radical polymerization reactions described herein.

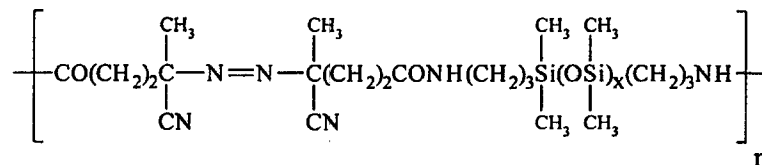
In the above described macroinitiator formulas, each Y is independently selected from the group consisting of those chemical moieties represented by the following formulas:



or combinations thereof; each of m, n, and p value are positive integers each independently having a value of 1 or greater, preferably m and p have values independently from about 14 to about 700, whereas n has no upper value except that it should not be so large as to limit applicability for practical reasons (viscosity, processing, solvent compatibility, etc.) during the polymerization reaction of the silicone-containing adhesive block copolymers, but is preferably a value of from about 1 to about 10.

The number average molecular weight of silicone-containing macroinitiator is from about 500 grams/mole to about 500,000 grams/mole, preferably from about 2,000 grams/mole to about 250,000 grams/mole, more preferably from about 5,000 grams/mole to about 100,000 grams/mole.

Preferred are the silicone-containing macroinitiators wherein Y is an azo group, even more preferably those silicone-containing macroazoinitiators corresponding to the following formula:



wherein x is an integer having a value of from about 50 to about 150, and n is an integer having a value of from about 4 to about 12, more preferably from about 6 to

about 9. Most preferred are those macroazoinitiators represented by the above formula wherein x is an integer having a value of either about 135 or 67, and n is an integer having a value of from about 6 to about 9.

The silicone-containing blocks (Block A) of the block copolymers herein preferably contain at least about 10 repeating monomer units, more preferably at least about 40 monomer units, even more preferably at least about 60 monomer units, wherein each of the repeating monomer units are derived from the select silicone-containing macroinitiators described herein, and the average molecular weight of each silicone-containing block preferably ranges from about 500 grams/mole to about 60,000 grams/mole, more preferably from about 1,000 grams/mole to about 25,000 grams/mole, even more preferably from about 2,000 grams/mole to about 15,000 grams/mole.

Ethylenically Unsaturated Monomer

The silicone-containing adhesive block copolymers of the hairspray composition herein comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90%, by weight of a copolymerizable ethylenically unsaturated monomers.

The blocks (block B) in the silicone-containing adhesive block copolymer are derived from ethylenically unsaturated monomers, wherein block B has a glass transition temperature (T_g value) of more than about -20°C, more preferably more than about -5°C, and also preferably less than about 60°C, more preferably less than about 50°C, and even more preferably less than about 40°C.

The ethylenically unsaturated monomers are copolymerizable with the silicone-containing macroinitiators and contain at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted. Preferred are vinyl monomers. Either a single type of ethylenically unsaturated monomer or combination of two or more ethylenically unsaturated monomers can be used. The ethylenically unsaturated monomers are selected to meet the requirements of or preferences for the silicone-containing adhesive block copolymers described herein, including solubility in the selected alcohol solvent, glass transition temperatures within the above-described ranges for hair styling or conditioning performance, reactivity with the selected silicone-containing macroinitiator, and so forth.

The ethylenically unsaturated monomers for use in making the silicone-containing adhesive block copolymers may be hydrophilic or hydrophobic, water soluble or water insoluble. These ethylenically unsaturated monomers are preferably hydrophilic monomers, or combinations of hydrophilic and hydrophobic monomers

provided that the resulting block copolymer in the hairspray composition has the requisite solubility and other characteristics defined herein. The term "hydrophilic monomers" as used herein refers to monomers which form water soluble homopolymers, whereas the term "hydrophobic monomers" as used herein refers to monomers which form water-insoluble polymers. In this context, the term "water soluble" means that the polymer is soluble in water, ethanol, n-propanol, isopropanol, or combinations thereof, at a concentration of at least about 0.1mg/ml, preferably at a concentration of at least about 0.5mg/ml, even more preferably at a concentration of at least about 1mg/ml, at 22.7°C.

The ethylenically unsaturated monomers when copolymerized into repeating units or blocks (block B) in the silicone-containing adhesive block copolymer herein preferably contains at least about 10 repeating monomers, more preferably at least about 20 repeating monomers, even more preferably at least about 50 repeating monomer units.

Nonlimiting classes of ethylenically unsaturated monomers useful herein include unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and combinations thereof.

Some examples of suitable ethylenically unsaturated monomers include, but are not limited to, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, acrylic and methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol,

methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols preferably having from about 1 to about 12 carbon atoms; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxylmethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the free radical copolymerization reaction with the macroinitiator described hereinafter.

Preferred ethylenically unsaturated monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

Neutralized Block Copolymers

The silicone-containing adhesive block copolymers may comprise acidic functionalities, such as carboxyl groups, and are usually used in at least partially neutralized form to promote solubility or dispensability of the block copolymer in the alcohol solvent defined herein. In addition, use of the neutralized form aids in the ability of the hair styling spray compositions to be removed from the hair by shampooing. The extent of such neutralization ranges from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from about

40% to about 85%, neutralization of the acidic functionalities of the silicone-containing adhesive block copolymer.

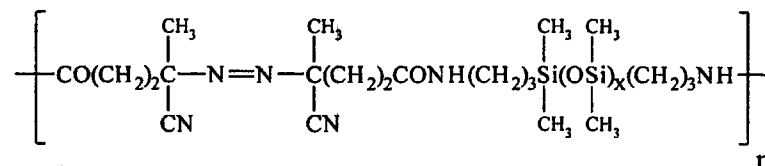
Neutralization of the silicone-containing adhesive block copolymer containing acidic functionalities may be accomplished by any conventional or otherwise known technique for affecting such neutralization by using an organic or inorganic base material. Metallic bases are particularly useful for this purpose. Suitable base neutralizers include, but are not limited to, ammonium hydroxides, alkali metal hydroxides, or an alkaline earth metal hydroxides, preferably potassium hydroxide and sodium hydroxide. Examples of other suitable neutralizing agents include, but are not limited to, amines or amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA) and dimethyl stearamine (DMS) and combinations thereof. Preferred are amines and metallic bases.

Neutralization of silicone-containing adhesive block copolymer containing basic functionalities, e.g., amino groups, are likewise preferably at least partially neutralized with an organic or inorganic acid e.g., hydrogen chloride. Neutralization can be accomplished by any conventional or otherwise known technique for accomplishing such neutralization. The preferred extent of neutralization is the same as that described for neutralization of acidic functionalities.

Solubility of the selected silicone-containing adhesive block copolymer, if the selected copolymer contains an acidic or basic functionality, should be determined after the desired acid or base neutralization.

Preferred Silicone-Containing Adhesive Block Copolymers

Nonlimiting examples of preferred silicone-containing adhesive block polymers include, but are not limited to, the following block copolymers derived from the macroazoinitiators which conform to the following formula.



[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)]_n

t-butyl acrylate: 40%; n-butyl acrylate: 28%; acrylic acid: 12%; methacrylic acid: 10%;

silicone macroazoinitiator (above-described formula, $x=135$, n is from about 6 to about 9) 10%;

Molecular weight of silicone block: 10,000 grams/mole

Polymer molecular weight: 114,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 40%; n-butyl acrylate: 24%; acrylic acid: 21%;

silicone macroazoinitiator (above-described formula, $x=135$, n is from about 6 to about 9) 15%;

Molecular weight of silicone block: 10,000 grams/mole.

Polymer molecular weight: 86,000 grams/mole.

[Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)] $_n$

t-butyl acrylate: 32%; ethyl acrylate: 33%; acrylic acid: 20%;

silicone macroazoinitiator (above-described formula, $x=67$, n is from about 6-9) 15%.

Polymer molecular weight: 110,600 grams/mole.

Molecular weight of silicone block: 5000 grams/mole.

The preferred silicone-containing macroazoinitiators described above are available from Wako Chemical USA, Inc., Richmond, Virginia, USA as VPS1001 and VPS 0501 (poly(dimethylsiloxane) initiators).

Properties of the Dried Hairspray Compositions

The hairspray compositions of the present invention, when dried, preferably have specific physical properties as defined by cohesive strength, total energy absorption per unit area, impact strength and improved removeability (defined in terms of hair stiffness and flaking values). Each of these preferred physical properties is described in detail hereinafter.

Cohesive Strength (kgf/mm²)

Cohesion is the strength of the bonds formed within a sample, e.g., a dried hairspray composition. The cohesive strength, which is designated as kgf/mm² (kilograms of force per square millimeter) is the maximum unit stress a material will

withstand when being subjected to displacement in tension. Stress is the ratio of measured load (kg X f) to the original cross-sectional area (mm²) of the sample.

The cohesive strength of dried hairspray compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 638-91, Standard Test Method for Tensile Properties of Plastics, Published January 1992, herein incorporated by reference in its entirety. The following test method to measure cohesive strength is similar to the ASTM standard, however, several modifications are made to better represent the tensile properties of the dried hairspray films. The measurements are made at about 22.7°C and about 50% relative humidity. The test method, described herein specifically uses a modified dumbbell shape with a thickness equal to about 0.4 mm., and uses an Instron Model Mini-55 (available from Instron Corp., Canton, MA) as the testing machine for applying the force to the polymer film samples.

A dried film sample is prepared by drying an amount of the hairspray composition (i.e., the silicone-containing adhesive copolymer and solvent selected from the group consisting of water, ethanol, n-propanol, isopropanol, and mixtures thereof, and any additional optional components) in a flat-bottomed aluminum mold coated with PFA (perfluoroalkoxy) Teflon®. The copolymer film is dried at about 22.7°C and about 50% relative humidity until film has attained a "constant weight". By "constant weight" is meant that there is less than a 1% weight fluctuation in the sample over a period of 24 hours. The drying film should be kept in an area protected from air currents, which could result in non-uniform drying and formation of air bubbles. The copolymer film is cut into a dumbbell shape for testing. The sample should be substantially free of defects, i.e. cracks, chips, tears, etc. Figures 1 and 2 illustrate the planar dumbbell shaped film to be used in the tensile testing described herein for the cohesive strength and the total energy absorption per unit volume. Figure 1 illustrates an overhead view of the dumbbell shaped sample. Figure 2 illustrates a cross section through the dumbbell shaped sample. The width of the narrow section, 1, of the dumbbell is about 3 mm (1 = 3 mm). The length of the narrow, 3 mm., section of the dumbbell, 3, is about 13 mm. (3 = 13 mm.). The gauge length of the narrow section, 2, is the initial film length used in the determination of the strain of the sample. The gauge length is equal to or less than the length of the narrow section, preferably equal to the length of the narrow section (i.e., 2 = 3). The width of the ends of the dumbbell, 4, are about 10 mm. (4 = 10 mm.). The distance between end sections of the film, 5, is about 28 mm. (5 = 28 mm.). The overall length of the film, 6, is about 64 mm. (6 = 64 mm.). The length of the wide ends of the film is about 18 mm. ((6-5)/2 = 18 mm.). The transition

sections between the wide ends and the narrow section of the film are about 6.5 mm. in length (i.e. $(5-3)/2 = 6.5$ mm.). Also the end portions of the narrow, center portion should be smoothly curved to avoid any stress points in the sample. The curve of the transition section, should have a radius, r , of from about 0.5 in. to about 5 inches, and should join tangentially to the narrow section. The film is formed to a thickness, t , of 0.4 mm. ($t = 0.4$ mm.). The dumbbell shaped samples are further equilibrated to a "constant weight". By "constant weight" is meant that over a selected 4 day period, there is no more than 0.2% average weight gain or loss, relative to the dumbbell's measured weight 4 days previous and no more than $\pm 0.2\%$ weight drift should be observed between two consecutive measurements in the four day period of time. The dumbbell should be tested within a 7 day period of reaching this constant weight.

The samples are tested on a calibrated Instron Model Mini-55 tensile tester. Before mounting the sample into the Instron, the length, L , width, W , and thickness, t , of the narrow section of the dumbbell shaped sample are measured to the nearest micron with a calibrated micrometer. The dimensional measurements are required by the Instron for force per unit area calculations. The wide ends of the dumbbell samples are clamped into the Instron and pulled at a crosshead rate of 5 mm. per minute. The Instron tester measures the overall forces (e.g., kgf) applied to the film. These forces are spread over the cross sectional area of the narrow section of the film. The cohesive strength of the copolymer is the maximum unit force measured by the Instron divided by the cross sectional area of the narrow portion of the film.

The dried hairspray compositions of the present invention have a cohesive strength of greater than about 0.5 kgf/mm^2 , preferably greater than about 0.6 kgf/mm^2 , and more preferably greater than about 0.7 kgf/mm^2 .

Total Energy Absorption Per Unit Volume (e.g., kgfmm/mm^3)

The total energy absorption per unit volume, which is designated as kgfmm/mm^3 (kilograms of force millimeters per millimeter cubed), is the ratio of the total energy required to reach the autobreak point (in $\text{kgf} \times \text{mm}$) to the original volume of the sample (mm^3). The total energy required to reach the break point is calculated using standard techniques by determining the area under a load versus displacement curve for the sample. The total energy absorption per unit volume is also known as "toughness" by those skilled in the art of polymer science and materials testing.

The measurements are made at about 22.7°C and about 50% relative humidity.

The dried hairspray compositions of the present invention preferably have a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm^3 ,

more preferably greater than about 0.75 kgfmm/mm³, even more preferably greater than about 1.10 kgfmm/mm³, and most preferably greater than about 2.15 kgfmm/mm³.

Impact Strength

Impact strength is the mean-failure energy (mass X gravity X height) required to produce sample failure, e.g., in a dried hairspray composition. The sample failure is characterized by a crack or split created by the impact of the falling weight that can be seen by the naked eye under normal laboratory lighting conditions.

The impact strength of the dried hairspray compositions of the current invention are determined using the following method. This method is based on ASTM Designation: D 5420-93, Standard Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact), Published 1995, herein incorporated by reference in its entirety, however, several modifications are made to better represent the impact properties of the dried film. The measurements are made at about 22.7° C and about 50% relative humidity.

The test method, described herein specifically uses rectangular shaped samples with a thickness equal to about 0.4 mm, and uses a GCA/Precision Scientific Penetrometer modified to drop a blunt faced probe to a distance of 70 mm and equipped with a Precision Scientific solenoid controller for GCA Penetrometer, a blunt faced cylindrical probe with a surface area of 8 mm² (OK M&T Corp. - part # WSU30), and a ruler which measures in 1 mm increments.

The samples are prepared using the film drying method described above in the cohesive strength measurements. The copolymer film is cut into the rectangular shape, e.g. 10 mm X 20 mm. The thickness of the sample is 0.4 mm. The film thickness of various test samples should be maintained within $\pm 15\%$ of 0.4 mm.

The following measurement process is used. Turn on the solenoid operated probe release controller. The controller should begin to cycle on and off as indicated by a red light. Be sure the probe face is flush with the impact surface so that the sharp edge of the probe does not strike the film. Place a film sample on the Impact Tester over the target area. Direct the metric ruler gently on the film sample. Direct the lightening source across the surface of the sample such that the light source is in the same plane as the surface of the film. Small fractures in the film will reflect light and be easily detected. Move the probe up to desired drop distance. A suggested distance progression is: 1 mm, 3 mm, 5 mm, 10 mm, 15 mm, 20 mm, 25 mm, and further 5 mm increments up to 70 mm. (70 mm is the upper limit of the instrument).

Turn on the instrument switch, to drop the probe onto the sample. The first step in the measurement of impact energy is to find the range of probe height necessary to fracture the film. Start at 1 mm for the first step. Continue to move up according to the suggested distance progression until a fracture is observed. When a fracture is observed make a note of it and move to a new sample. The second step in determining impact energy is to set a new sample and start drop at an observed fracture point in the range procedure. Set a new film sample and move the probe to the next lowest setting. If the film fractures, record result and repeat previous step. If the film does not fracture, set a new sample and move to the next distance. Continue to set new samples and increase the drop distance until the film fractures. Continue the procedure until 5 fractures are observed. Calculate the amount of work energy, i.e. the fracture strength using the following formula:

$W = m \times g \times h$, where

W = amount of work energy in ergs,

m = mass of probe (59.53 g) (The probe is removable and can be replaced with one of different mass or impact surface area).

g = gravitational constant (980.665 cm/sec²),

h = average distance probe travels to impact (cm).

The dried hairspray compositions of the present invention preferably have an impact strength of greater than about 7000 ergs, more preferably greater than about 20,000 ergs, and even more preferably greater than about 50,000 ergs.

Hair Spray Removeability

The adhesive copolymers herein have improved removeability when used in the preferred hairspray embodiments of the present invention. In this context, improved removeability means that the adhesive copolymers are more easily removed from the hair or other applied surface during shampooing.

For purposes of defining the preferred hair spray compositions of the present invention, removeability is determined indirectly by evaluating hair stiffness and the appearance of observable white flakes after treating the hair in accordance with the removeability methodology described hereinafter. It has been found that the removeability of a hair spray formulation after shampooing correlates with the resulting stiffness/softness of the hair and the appearance/nonappearance of white flakes on the hair after a series of shampooing cycles. The hair spray compositions of the present invention have high removeability e.g., reduced stiffness and reduced white flaking. The term "removeability" as used herein therefore refers to hair

stiffness values (0-4 scale) and white flaking values (0-4 scale) as measured in accordance with the methodology described hereinafter.

For purposes of the defining the preferred hair spray compositions of the present invention, the removeability of the hair spray compositions is defined as a combination of hair stiffness values and hair flaking values, wherein the hair spray compositions provide hair flaking values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0, and hair stiffness values ranging from 0 to about 3.5, preferably from 0 to about 2.5, more preferably from 0 to about 2.0.

Methodology: Hairspray Removeability

Removeability of the hairspray composition of the present invention, as indirectly evaluated in terms of hair stiffness and the appearance of white flakes, is determined in accordance with the following methodology. The methodology simulates multiple application and multi-cycle application of hairspray compositions so as to indirectly determine how readily and effectively such hairspray compositions are removed from hair.

The methodology described herein provides a means of evaluating hair switches blindly treated with hairspray embodiments of the present invention. The method by which each hair switch is treated with the hairspray embodiments, and the method by which each treated hair switch is then evaluated for removeability are described in detail below.

Two trained panelists each evaluate identically treated hair switches or sets of hair switches for stiffness and the appearance of white flakes. The panelists then individually assign each of the treated hair switches with a numerical score (0 to 4 scale) for hair stiffness and a numerical score for flaking (0 to 4 scale). The order in which the hair switches are treated with different hair spray embodiments is randomized and conducted round robin. Two identical sets of switches are prepared as described below for each panelist so that each has a fresh set of switches to evaluate. Before evaluating the blindly treated hair switches, each panelist also evaluates (not blinded) an untreated hair switch as a zero reference for hair stiffness and flaking. Each panelist also evaluates a control treated hair switch as a flaking reference (score 4.0) and another control treated hair switch as a hair stiffness reference (score 4.0). The hair stiffness values as defined herein are determined by averaging the hair stiffness scores provided by the two panelist. Likewise, the hair flaking values as defined herein are determined by averaging the hair flaking scores provided by the two panelists.

The hair switches are treated with either an aerosol or non-aerosol hair spray embodiment of the present invention in accordance with the following steps. The hair stiffness reference and the flaking reference are also prepared in accordance with the following steps, except that each is treated with the corresponding hair spray formulations as described hereinafter in Tables 2 and 3.

- 1) Vertically suspend a clean hair switch (10 inch European virgin brown hair, 20 gram) from its bound end and comb (black rubber comb, 5 inches by 1 inch, 1/2 fine tooth) through the switch to remove any tangles.
- 2) If necessary, use a static gun to eliminate any static build-up on the switch.
- 3) For non-aerosol products, spray the switch from a distance of 4 inches while applying ten pumps of the product to the switch and while moving the atomized spray pattern in a fluid up-and-down motion to cover the entire switch, or for aerosol products, spray each switch from a distance of 6 inches while applying the aerosol stream to the switch for a period of 3 seconds and while moving the aerosol stream in a fluid up-and-down motion to cover the entire switch.
- 4) Repeat step 3 on the opposite side of the switch.
- 5) After spraying the opposite side of the switch, hang the treated switch from its bound end to allow it to dry for one hour at ambient temperature, pressure and humidity.
- 6) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
- 7) Repeat steps 1 through 6.
- 8) Wet the treated hair switch with water (+15-20 grain hardness, 38°C, 1 gal/min. water pressure).
- 9) Apply 1 ml of shampoo (Table 1: methodology shampoo) along the length of the front of the wet hair switch and apply another 1 ml of the shampoo along the length of the reverse side of the wet hair switch.
- 10) Gently milk the switch from top to bottom (hand over hand between thumb and fingers) for 15 seconds at 1 stroke per second.
- 11) Rinse the hair switch with water (38°C, +15-20 grain hardness, 1 gal/min. water pressure) for 15 seconds. Gently squeeze the hair between the first and

- second fingers, drawing the fingers down the switch after 5 seconds, 10 seconds, and after final rinse.
- 12) Hang the treated switch and allow it to dry for two hours at 60°C in a hot box.
 - 13) Remove the dried switches from the hot box.
 - 14) Comb the dried switch using a black rubber comb (5 inches x 1 inch, 1/2 inch fine tooth) by combing away from the bound end of the switch but by initially starting toward the unbound end taking smaller strokes and then gradually taking larger strokes until the comb passes through the entire unbound length of the treated switch.
 - 15) Repeat steps 1-14.
 - 16) Repeat steps 1-13.
 - 17) A panelist then evaluates the treated switch by feeling it between their first and second fingers of their dominant hand and between their thumb and other fingers for stiffness and resistance to bending, and then assigns to the treated switch a hair stiffness score (0 to 4 scale). The value of the assigned score is relative to the hair stiffness reference score (4) and the untreated reference score (0).
 - 18) The panelist then combs the evaluated switch in accordance with the procedure set forth in Step 14 above, and then visually evaluates the combed switch for white flakes, coating, and white haze and assigns it a hair flaking score (0 to 4 scale). The value of the assigned score is relative to the hair flaking reference score (4) and the untreated reference score (0).

Table 1: Methodology Shampoo

Ingredient List	Percent Composition As Added	Percent Composition Chemical Content
Sodium Laureth Sulfate	40.0000	10.0000
Water - USP Purified	30.3000	30.3000
Sodium Lauryl Sulfate	29.1000	8.0025
Cocamide DEA	.5000	.4000
Kathon CG	.1000	.0015
Citric Acid Solution (50% active)	** adj. from 0 - 1% (note: water level qs. to 100%)	

Table 2: High Flaking Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	4.50	4.50
Water - USP Purified	15.50	15.50
Ethanol (SDA 40)	80.00	80.00

Table 3: High Stiffness Control

Raw Materials	Percent Composition As Added	Percent Composition Chemical Content
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (National Starch lot AF-6713)	6.00	6.00
Aminomethylpropanol, 95%	1.04	0.99
Water - USP Purified	15.50	15.50
Diisobutyl Adipate	0.20	0.20
Ethanol (SDA 40)	80.00	80.00

Each of the formulations described in Tables 1-3 are prepared by conventional formulation and mixing techniques.

Optional Ingredients

The hairspray compositions of the present invention may further comprise one or more optional ingredients known or otherwise effective for use in hairsprays and other hair styling compositions. These optional ingredients may be used to improve or otherwise modify aesthetics, performance or stability of the hairspray compositions. Concentrations of such optional ingredients will vary with the type of material added and its intended performance, but will typically and collectively range from about 0.005% to about 50%, more typically from about 0.05% to about 30% by weight of the composition.

Plasticizers for the silicone-containing adhesive block copolymer are especially useful in the hairspray herein. Suitable plasticizers include any known or otherwise effective plasticizer suitable for use in hair care or other personal care compositions, nonlimiting examples of which include glycerin, diisobutyl adipate, butyl stearate, propylene glycol, tri-C₂-C₈ alkyl citrates, including triethyl citrate

and tri-propyl, -butyl, -pentyl, etc., analogs of triethyl citrate, and combinations thereof. Preferred is triethyl citrate.

Plasticizers are typically used at concentrations of from about 0.01% to about 10%, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%, by weight of the hairspray composition. Preferably, the weight ratio of silicone-containing block copolymer to the plasticizer is from about 1:1 to about 40:1, preferably from about 2:1 to about 30:1, more preferably from about 3:1 to about 25:1.

Other optional ingredients include an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hairspray composition. Preferred are minimum concentrations of at least about 0.01% by weight of the hairspray composition, and maximum concentrations sufficiently low for the selected system that the silicone-containing adhesive block copolymer remains solubilized or otherwise dispersed in the hairspray composition. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the solubility of the silicone-containing adhesive block copolymer in the hairspray composition will decrease until it is no longer soluble or dispersible in the composition and will precipitate out of the composition. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifier, alcohol solvent, other liquid vehicles, block copolymer, and other ingredients present in the composition. Concentrations of the optional ionic strength modifier are typically range from about 0.01% to about 4%, preferably from about 0.01% to about 2%, more preferably from about 0.01% to about 0.1%, by weight of the composition

The optional ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The optional ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the

composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the hairspray composition. The ionic strength modifiers can be incorporated into the hairspray compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. When such an optional ionic strength modifier system is used, it is a necessary that both anions and cations of the optional ionic strength modifier system be included in the hairspray composition.

Nonlimiting examples of suitable optional cations for use in the compositions are alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, more preferably sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below. Other nonlimiting examples of suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and triethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

Other optional ingredients include surfactants (which may be anionic, cationic, amphoteric, or zwitterionic and which include fluorinated surfactants and silicone copolyols), propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.); emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene

cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents; sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

Hairspray Products

The hairspray compositions of the present invention are dispensed as sprayed or atomized liquids from any container or package known or otherwise effective for providing such delivery. Such containers or packages will typically be in the form of pump spray dispensers or aerosol canisters, both of which are well known to those skilled in the art.

The hairspray compositions of the present invention further comprises a propellant when dispensed from a pressurized aerosol container. Any propellant or combination of propellants known or otherwise effective for use in such containers, and which are suitable for application to human skin or hair, can be used herein. Suitable propellants include liquifiable gases conventionally used for aerosol containers, most typically volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane, isobutane, and combinations thereof.

Other suitable propellants include hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other suitable propellants include dimethylether, nitrogen, carbon dioxide, nitrous oxide, atmospheric gas, and combinations thereof. Preferred are the hydrocarbon propellants and combinations of hydrocarbon propellants, especially isobutane and combinations containing isobutane.

The aerosol propellant may be mixed with the present hairspray compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the concentration of propellant is from about 10% to about 60%, preferably from about 15% to about 50% , by weight of the total hairspray composition including the propellant.

Other suitable containers or packages include those pressurized aerosol dispensers where the propellant is separated from contact with the hairspray composition. An example of such a package or container would be a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Examples of such dispensers are described in U.S.

Patent 4,077,441, March 7, 1978, Olofsson; U.S. Patent 4,850,577, July 25, 1989, TerSteg; and U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, which descriptions are incorporated herein by reference. The hairspray compositions of the present invention may also be dispensed in any known or otherwise effective means for delivery to the hair, including any known or otherwise effective atomizing means such as a nonaerosol pump spray device.

Method of Making

The hairspray compositions of the present invention can be made using conventional formulation and mixing techniques. For example, the silicone-containing adhesive block copolymer and the alcohol solvent are combined and mixed together to form a homogeneous solution or dispersion. Other ingredients are then added to the homogenous solution or dispersion and mixed to yield the hairspray composition of the present invention. If the silicone-containing adhesive block copolymer is neutralized, the neutralizer is preferably added prior to addition of other ingredients. The hairspray composition is then packaged in a conventional or otherwise suitable mechanical pump spray device, or alternatively, in the case of aerosol hairspray compositions, the hairspray composition is packaged in a conventional or otherwise suitable aerosol canisters along with an appropriate propellant system.

Method of Use

The hairspray compositions of the present invention may be used in a conventional manner to provide the desired hair styling benefits. Such methods generally involve application of an effective amount of the composition to dry hair which has been arranged or positioned in the desired style. In this context, the term "effective amount" means an amount sufficient to provide the hair hold and style benefits desired, typically an amount ranging from about 0.5 grams to about 30 grams of the composition, depending upon the selected hairspray composition and formulation, dispenser type, length of hair, type of hair style, and so forth. The composition is applied to the hair by spraying or atomizing the composition using a mechanical pump spray device, a pressurized aerosol container, or other appropriate delivery means. The composition is then dried or allowed to dry on the applied surface.

The following Experiments and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as

many variations of the invention are possible without departing from its spirit and scope.

EXAMPLES

The following non-limiting examples illustrate specific embodiments of the hairspray compositions of the present invention, and methods of providing hair styling benefits to dry hair using the compositions. It is understood, however, that various additions or modifications of the specific exemplified embodiments can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of the subject invention.

The following exemplified polymers 1.1 and 1.2 are specific silicone-containing adhesive block copolymers suitable for use in the hairspray compositions of the present invention. Each of these exemplified block copolymers are then incorporated into specific hairspray embodiments of the present invention as Examples 2.1, 2.1, 2.3.

Polymer 1.1

[Poly(dimethyl siloxane)-block-poly(t-butylacrylate-co-acrylic acid)]_n.

Place 62.4 parts of t-butyl acrylate, 20.8 parts acrylic acid, 200 parts acetone (as a solvent), and 15 parts isopropanol (as a chain transfer agent) in a roundbottom flask. Separately, dissolve 16.8 parts VPS-1001(poly(dimethyl siloxane)initiator) macroazoinitiator (commercially available from Wako Chemical USA, INC., Richmond, VA) into 200 parts ethyl acetate and add the solution to an addition funnel. Purge the reaction vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction mixture to 58°C. Add the VPS-1001 solution to the reaction flask in a dropwise fashion over the course of one hour. Maintain heating and stirring for 20 hours. Terminate the reaction by opening the reactor to the atmosphere and cooling to room temperature.

The block copolymer is precipitated from the solution by adding one part of the polymer solution to 15 parts water. The resultant polymer is redissolved in acetone and is precipitated again from 15 parts water. The resultant block copolymer is then placed in a vacuum oven for heated drying. Following the drying, the polymer is ground and extracted for 20 hours with hexane using a soxhlet extractor. The polymer is then vacuum dried with heat in an oven. The glass transition

temperature of the block B of the resulting polymer is between about -20°C and 60° C.

Polymer 1.2 [Poly(dimethyl siloxane)-block-poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)]_n

Place 80 parts of t-butyl acrylate, 56 parts n-butyl acrylate, 12 parts acrylic acid, 10 parts methacrylic acid, 400 parts acetone (as a solvent), and 50 parts isopropanol (as a chain transfer agent) in a roundbottom flask. Separately, dissolve 20 parts VPS-1001(poly(dimethyl siloxane)initiator) macroazoinitiator (commercially available from Wako Chemical USA, INC., Richmond, VA) into 400 parts ethyl acetate, add to this solution 12 parts acrylic acid and 10 parts methacrylic acid, and add the solution to an addition funnel. Purge the reaction vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction mixture to 58°C. Add the VPS-1001 solution to the reaction flask in a dropwise fashion over the course of one hour. Maintain heating and stirring for 20 hours. Terminate the reaction by opening the reactor to the atmosphere and cooling to room temperature.

The block copolymer is precipitated from the solution by adding one part of the polymer solution to 15 parts water. The resultant polymer is redissolved in acetone and is precipitated again from 15 parts water. The resultant block copolymer is then placed in a vacuum oven for heated drying. Following the drying, the polymer is ground and extracted for 20 hours with hexane using a soxhlet extractor. The polymer is then vacuum dried with heat in an oven. The glass transition temperature of the block B of the resulting polymer is between about -20°C and 60° C.

Example 2

The following examples represent specific aerosol hairspray embodiments of the present invention.

	<u>Example Number</u>					
Component (wt%)	2.1	2.2	2.3	2.4	2.5	2.6
Copolymer 1.1	5.00	4.00	3.50	---	---	---
Copolymer 1.2	---	---	---	5.00	4.00	3.50
Isododecane ¹	0.50	---	---	0.50	---	---
Triethyl citrate ²	--	--	0.21	--	--	0.21
Diisobutyl adipate	0.70	0.45	--	0.70	0.45	--

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Propylene glycol	--	--	0.30	--	--	0.30
Sodium hydroxide ³	1.00	--	--	1.00	--	--
Potassium hydroxide ⁴	--	0.94	1.20	--	0.94	1.20
Perfume	0.10	0.10	0.10	0.10	0.10	0.10
Water	QS100	QS100	QS100	QS100	QS100	QS100
Sodium Benzoate	0.10	0.10	--	0.10	0.10	--
Ethanol ⁵	56.69	57.42	72.0	56.69	57.42	72.0
Propellant - Isobutane	--	--	7.02	--	--	7.02
Propellant - n-butane	10.00	---	--	10.00	---	--
Propellant - Dimethyl ether ⁶	10.00	---	--	10.00	---	--
Propellant - Hydrofluorocarbon 152a ⁷	--	25.0	15.98	--	25.0	15.98

¹ PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

² CITROFLEX-2, from Morflex, Inc., Greensboro, NC, USA.

³ Sodium hydroxide is 30% active.

⁴ Potassium hydroxide is 45% active.

⁵ SDA 40 (100% ethanol).

⁶ DYMELE - A, from Dupont.

⁷ DYMELE-152a, from Dupont.

The exemplified hairspray compositions 2.1-2.6 are prepared as described above, by first mixing the silicone-containing adhesive block copolymer (polymer 1.1 or 1.2) with ethanol, neutralizing the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition. Propellants for aerosol embodiments are charged to aerosol containers after the remainder of the prepared composition has been added.

Example 3

The following examples represent nonaerosol hair spray compositions of the present invention.

Component (wt%)	<u>Example Number.</u>							
	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8
Copolymer 1.1	4.00	5.00	6.00	4.00	---	---	---	---
Copolymer 1.2	---	---	---	---	3.00	3.50	2.50	4.00
Isododecane ¹	1.00	---	---	---	---	1.0	2.0	---
Diisobutyl adipate	0.40	---	0.90	0.55	---	---	---	0.40
Sodium hydroxide ²	0.96	1.20	1.44	---	---	1.20	---	1.35
Potassium hydroxide ³	--	--	--	1.21	1.00	--	0.70	--
Perfume	0.10	0.10	0.10	0.10	0.10	0.15	0.10	0.15
Water	QS10	QS10	QS10	QS10	QS10	QS10	QS10	QS10
	0	0	0	0	0	0	0	0
Sodium Benzoate	--	--	--	--	0.10	0.10	--	0.10
Ethanol ⁴	76.54	71.95	81.56	71.25	79.40	69.26	78.00	55.00

¹ PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

² Sodium hydroxide is 30% active.

³ Potassium hydroxide is 45% active.

⁴ SDA 40 (100% ethanol).

The exemplified hairspray compositions 3.1-3.8 are prepared as described above, by first mixing the silicone-containing adhesive block copolymer (polymer 1.1 or 1.2) with ethanol, neutralizing the polymer with sodium or potassium hydroxide, then adding sequentially (as applicable) with mixing, isododecane, plasticizer, perfume, and water. If sodium benzoate is used, it is added after water addition. Most preferably a premix of water and sodium benzoate is made and then added after the main water addition.

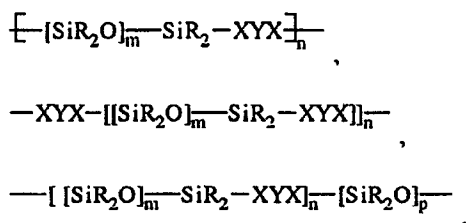
Each of the exemplified hairspray compositions in Examples 2 and 3 are specific embodiment of the hairspray compositions of the present invention, and provide improved hair styling performance when applied to dry, styled or positioned hair, and in particular provide improved maintenance or hold when applied to dry hair and causes minimal or no drooping of the hair during or immediately after application.

Each of the exemplified hair spray compositions in Examples 2 and 3 also provide improved removeability from hair, and when evaluated by the removeability methodology described herein, provide a hair stiffness value of less than 2.0 and a hair flaking value of less than 2.0.

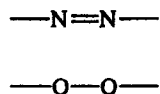
What is claimed is:

1. A hairspray composition comprising:

- (a) from about 50% to about 99.9% by weight of an alcohol solvent;
- (b) from about 0.1% to about 30% by weight of an adhesive block copolymer having a weight average molecular weight from about 10,000 grams/mole to about 10,000,000 grams/mole and which is formed from the free radical polymerization of an ethylenically unsaturated monomer with a silicone macroinitiator selected from the group consisting of



and combinations thereof, wherein each R is independently selected from the group consisting of C1-C10 alkyl, phenyl, C1-C10 alkyl-substituted phenyl, and mixtures thereof, X is a divalent radical, Y is selected from the group consisting of



and combinations thereof; and m, n, and p are positive integers independently having a value of 1 or greater; and

wherein the silicone macroinitiator has a number average molecular weight from about 500 grams/mole to about 500,000 grams/mole, and the ethylenically unsaturated monomers are copolymerizable and form one or more polymeric blocks within the adhesive block copolymer having a Tg value of from about -20 °C to about 60°C.

2. The hairspray composition of any one of the preceding claims wherein the alcohol solvent is selected from the group consisting of ethanol, n-propanol, isopropanol, and mixtures thereof, and wherein the adhesive block copolymer is solubilized in the hairspray composition.
3. The composition of either of any one of the preceding claims wherein the silicone macroinitiator is a silicone macroazoinitiator where Y is an azo group.
4. The composition of any one of the preceding claims wherein the block copolymers comprise from about 60% to about 95% by weight of the copolymerized ethylenically unsaturated monomers, and from about 5% to about 40% by weight of the copolymerized silicone macroinitiators.
5. The composition of any one of the preceding claims wherein m has a value of from about 14 to about 700, n has a value of from about 1 to about 10, and the silicone macroazoinitiator has a number average molecular weight of from about 5,000 grams/mole to about 100,000 grams/mole.
6. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about 0.5 kgf/mm^2 , a total energy absorption per unit volume of greater than about 0.55 kgfmm/mm^3 and an impact strength of greater than about 7000 ergs.
7. The composition of any one of the preceding claims wherein the composition, when dried, has a cohesive strength of greater than about 0.7 kgf/mm^2 , a total energy absorption of greater than about 1.10 kgfmm/mm^3 , and an impact strength of greater than about 50,000 ergs.

8. The composition of any one of the preceding claims wherein the vinyl monomer units are selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl toluene, butadiene, cyclohexadiene, ethylene, propylene n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and combinations thereof.

9. A composition according to any one of preceding claims wherein the composition provides a hair stiffness value of from 0 to about 2.5 and a hair flaking value of from 0 to about 2.5

10. A method of styling hair comprising the step of applying to dry, positioned hair an effective amount of the composition of any one of the preceding claims.

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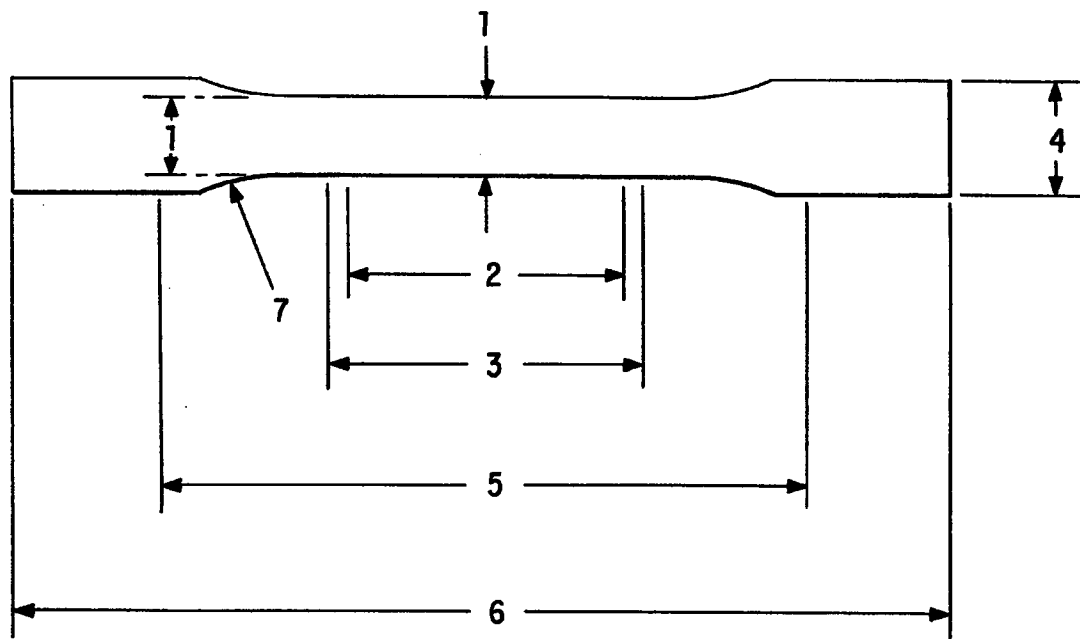


FIG. 1

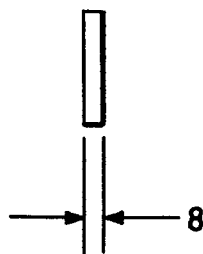


FIG. 2

INTERNATIONAL SEARCH REPORT

national Application No

PCT/IB 98/00784

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61K7/06 C08G77/442 C09D183/10 C08L83/10 C08F293/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08G C09D C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 766 957 A (WAKO PURE CHEMICAL IND.) 9 April 1997 cited in the application see column 7, line 52-56; claims 1-7 -----	1-10
A	EP 0 659 838 A (WACKER CHEMIE) 28 June 1995 see claims 1,2 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 August 1998

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04/09/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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			JP 9157339 A	17-06-1997
EP 659838	A	28-06-1995	DE 4338421 A	11-05-1995
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			CA 2118173 A	11-05-1995
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Bezeichnung:

Kosmetische Zubereitungen für Lacke und Wasserwellenlotionen auf der Basis von Blockmischpolymerisaten

71

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8 MÜNCHEN 86, POSTFACH 86 02 45

Anwaltsakte 26 660
Be/Ro

29. SEZ. 1975

L'OREAL
Paris / Frankreich

"Kosmetische Zubereitungen für Lacke und Wasserwellen-
lotionen auf der Basis von Blockmischpolymerisaten"

Erfinder: Christos PAPANTONIOU
Quintino GAETANI

Die vorliegende Erfindung betrifft kosmetische Zuberei-
tungen für Haare, im besonderen Lacke und Wasserwellen-
lotionen, die als Harz Blockmischpolymerisate enthalten.

MB/S.170

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Die Anmelderin hat bereits die Verwendung zahlreicher synthetischer Polymerisate und im besonderen die Verwendung bestimmter heterogener Polymerisate sowie bestimmte homogene Polymerisate für die Herstellung derartiger Zubereitungen vorgeschlagen.

Es wurde nunmehr gefunden, daß es ebenso möglich ist, ausgezeichnete Haarzubereitungen und im besonderen Lacke und Lotionen für Wasserwellen dadurch zu erhalten, daß man andere Polymerisatarten und namentlich Blockpolymerisate, und insbesondere Blockpolymerisate mit zwei oder drei Sequenzen besonderer Art verwendet.

Wie später noch ausgeführt, haben diese Polymerisate eine große Bedeutung, da es genügt, die Beschaffenheit der Sequenzen zu ändern, um Polymerisate mit unterschiedlichen Eigenschaften zu erhalten.

Diese Besonderheit der vorliegenden Blockpolymerisate hat einen großen Vorteil insbesondere bei der Herstellung von Zubereitungen in Form von Lacken oder Wasserwellenlotionen, da, wie bekannt, einige in wäßriger oder wäßrig-alkoholischer Lösung und andere nur in alkoholischer Lösung erhalten werden können.

Nachfolgend ist auf den Begriff der Blockpolymerisate einzugehen; es ist tatsächlich allgemein bekannt, daß unterschiedliche Monomeren, die Mischpolymerisate bilden, sich

in verschiedener Weise zur Bildung der polymeren Kette anordnen können, und daß allgemein Polymerisationsverfahren dahingehend eingestellt werden können, daß man verschiedene Typen von Polymerisaten erhält.

Im besonderen ist es mit einem genau bestimmten Polymerisationsverfahren möglich, Mischpolymerisate zu erhalten, deren Grundeinheiten nach der Species gruppiert sind, wobei diese Gruppierungen als "Sequenz" oder als "Block" bezeichnet werden.

Solche Mischpolymerisate werden im allgemeinen Blockmischpolymerisate bezeichnet.

Die Blockmischpolymerisate werden im allgemeinen aus zwei Polymerisaten gebildet, die in zwei oder drei Sequenzen auftreten, wobei jede Sequenz von gleichen Monomeren gebildet wird.

Es ist darauf hinzuweisen, daß die Anzahl der Sequenzen sich nach den vorgesehenen Verwendungen ändern können.

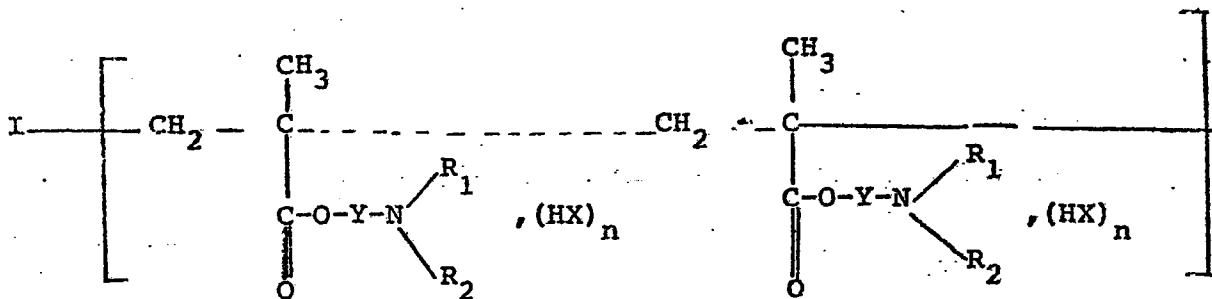
Im Rahmen der vorliegenden Erfindung sind die Mischpolymerisate Mischpolymerisate mit zwei oder drei Sequenzen, d.h. daß die Verteilung der monomeren Grundeinheiten oder der Sequenzen in der polymeren Kette wie folgt schematisch dargestellt werden kann:

XXX XXXZZZ ... ZZZ (1)

oder in der folgenden Weise:

XXX XXXZZZ ... ZZZXXX ... XXX (2)

Die vorliegende Erfindung betrifft demgemäß eine kosmetische Zubereitung zur Haarbehandlung, im besonderen Lacke und Wasserwellenlotionen, die dadurch gekennzeichnet ist, daß sie in einem geeigneten kosmetischen Träger wenigstens ein Mischpolymerisat mit zwei oder drei Sequenzen enthält, wobei es einerseits wenigstens eine Sequenz (A) der nachfolgenden allgemeinen Formel enthält:

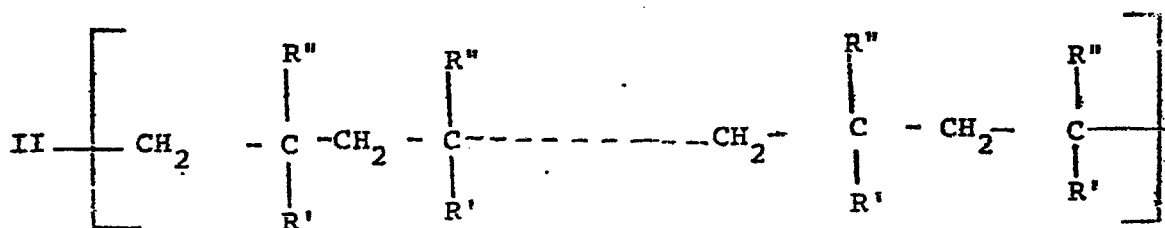


worin:

- Y eine gesättigte Kohlenwasserstoffkette mit 2 bis 4 Kohlenstoffatomen oder eine Kohlenwasserstoffkette mit 2 bis 4 Kohlenstoffatomen, die durch Heteroatome wie Schwefel oder Sauerstoff unterbrochen ist, darstellt,
- die Reste R₁ und R₂ gleich oder verschieden sind, und Alkylreste mit 1 bis 4 Kohlenstoffatomen sind,
- n = 0 oder 1 ist, und HX eine organische oder Mineralsäure, nämlich Salzsäure, Bromwasserstoffsäure, Milchsäure und/oder Essigsäure ist, und

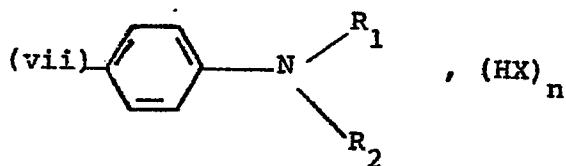
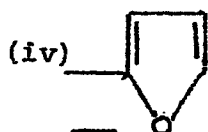
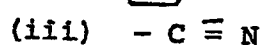
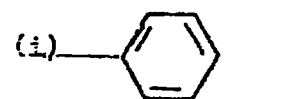
andererseits wenigstens eine Sequenz (B), die man durch Polymerisation eines auf anionischem Wege polymerisierbaren Monomers erhält.

Vorzugsweise weist die Sequenz (B), die man durch Polymerisation eines auf anionischem Wege polymerisierbaren Monomeren erhält, die nachfolgende allgemeine Formel auf:

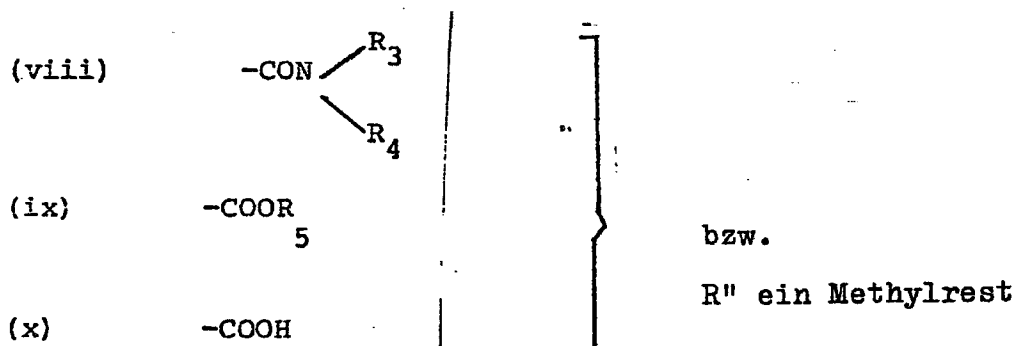


worin:

R' eine der nachfolgenden Gruppen ist, und



R'' ein Wasserstoffatom

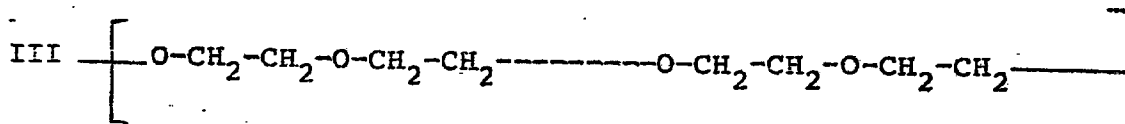


ist, worin:

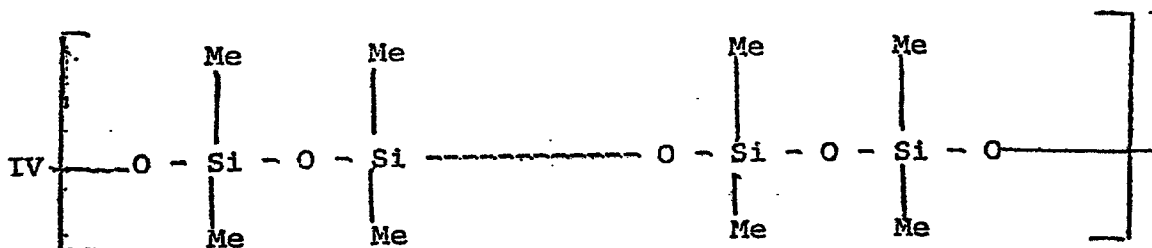
R_1 , R_2 , n und HX die gleichen Bedeutungen wie oben haben, R_3 eine gesättigte Kohlenwasserstoffkette mit 6 bis 18 Kohlenstoffatomen, R_4 ein Methyl- oder Äthylrest und R_5 eine gesättigte Kohlenwasserstoffkette mit 1 bis 18 Kohlenstoffatomen ist.

In einer bevorzugten Ausführungsform sind die Reste R' solche der Formeln wie unten unter (i) und (ix) angegeben.

In einer anderen Ausführungsform geht die Sequenz (B) aus der Polymerisation von Äthylenoxid hervor und kann durch die nachfolgende allgemeine Formel dargestellt werden:



In einer anderen Ausführungsform der Erfindung geht die Sequenz (B) aus der Polymerisation von Hexamethylcyclotrisiloxan oder Octamethyl-cyclo-tetrasiloxan hervor, und kann dargestellt werden durch die allgemeine Formel:



Unter Bezugnahme auf die oben angegebenen schematischen Formeln (1) und (2) können Polymerisate mit zwei oder drei Sequenzen die folgenden Formeln aufweisen:

- (i) AAA-BBB
- (ii) AAA-BBB-AAA oder
- (iii) BBB-AAA-BBB ,

worin die Sequenz (oder die Sequenzen) A der Formel I und die Sequenz (oder die Sequenzen) B der Formel II, III oder IV entsprechen.

Als Monomeren, die zur Bildung der Sequenzen A der Formel I führen können, sind die nachfolgenden Monomeren z.B. zu erwähnen:

Die Methacrylate von 2-(N,N-Dimethylamino)-äthyl, 2-(N,N-Diäthylamino)-äthyl, 2- $\sqrt{2}$ '-(N,N-Dimethylamino)-äthoxy-äthyl und 2- $\sqrt{2}$ '-(N,N-Diäthylamino)-äthoxy-äthyl.

Zu Monomeren, die zur Bildung der Sequenzen B der Formel II führen können, sind z.B. die nachfolgenden Monomeren zu erwähnen:

Styrol, 4-Methylstyrol, 2-Vinylpyridin, sein Chlorhydrat und sein Lactat, 4-Vinylpyridin, sein Chlorhydrat und sein Lactat, para-Dimethylaminostyrol, sein Chlorhydrat und Lactat, die Methacrylate von Methyl, Äthyl, Butyl, Hexyl, Octyl, Lauryl und Stearyl, Methacrylnitril, 2-Vinylfuran und N-Methyl-N-lauryl-methacrylamid.

Wenn der Rest R' in der Sequenz B der Formel II eine Carbonsäurefunktion vorstellt, kann diese Funktion mit Hilfe einer Mineral- oder organischen Base neutralisiert werden, wie mit Ammoniak, Monoäthanolamin, Diäthanolamin, Triäthanolamin, Isopropanolaminen, Morpholin, 2-Amino-2-methyl-1-propanol, 2-Amino-2-methyl-1,3-propandiol oder die Funktion kann weiterhin in die Form des Natrium-, Kalium- oder Magnesiumsalzes überführt sein.

In einer bevorzugten Ausführungsform der Erfindung können die tertiären Aminfunktionen der Sequenzen A der Formel I (wobei $n = 0$ ist) mit Hilfe eines Quarternisierungsmittels quarternisiert werden, beispielsweise mit Dimethylsulfat, Äthylbromid und β -Bromäthanol.

Der Prozentsatz der quarternisierten tertiären Aminfunktionen kann von 0 bis 100 % variieren, wobei der Quarternisierungsgrad im Hinblick auf die Bestimmung des Blockpolymerisats ausgewählt sein kann.

Weiterhin können, wie die Formel I ($n = 1$) dies zeigt, ein

Teil oder alle tertiären Aminfunktionen der Sequenzen A der Formel I mit Hilfe einer Mineralsäure oder organischen Säure in die Salzform überführt sein.

Im Hinblick auf die quarternären tertiären Aminfunktionen kann der Prozentsatz der in die Salzform überführten Funktionen von 0 bis 100 % variieren.

Wenig quarternisierte oder in die Salzform überführte Blockmischpolymerisate werden vorzugsweise in Lackaerosolen verwendet, während höher quarternisierte oder in die Salzform überführte Blockmischpolymerisate vorzugsweise in wässrigen oder wässrig-alkoholischen Wasserwellenlotionen verwendet werden.

Die Molekulargewichte der nach der vorliegenden Erfindung verwendeten Polymerisate mit zwei und drei Sequenzen können innerhalb weiter Grenzen variieren. Sie werden im allgemeinen im Hinblick auf ihre Bestimmung festgelegt, d.h. für Lacke oder für Wasserwellenlotionen.

Die Polymerisate mit bi- und tri-Sequenzen nach der vorliegenden Erfindung haben im allgemeinen Molekulargewichte zwischen etwa 1000 und 1.000.000, aber vorzugsweise zwischen 2000 und 300.000.

Es wurde bereits angegeben, daß die Zubereitungen der Erfindung in verschiedenen Formen und insbesondere in Form von Wasserwellenlotionen, in Form von Lacken oder weiterhin

in Form von Behandlungszubereitungen dargeboten werden können.

Beispielsweise kann ein Aerosollack für die Haare dadurch erhalten werden, daß man in einem Aerosolbehälter 0,2 bis 5 Gew.% Blockpolymerisat nach der Erfindung, 0 bis 35 und vorzugsweise 0 bis 25 Gew.% Alkohol und 60 bis 99,8 Gew.% unter Druck verflüssigtes Treibgas, wie Dichlordifluormethan und Trichlorfluormethan und ihre Gemische konditioniert.

Als einen solchen Alkohol verwendet man vorzugsweise Äthylalkohol oder Isopropylalkohol.

Eine Lotion für Wasserwellen nach der Erfindung kann beispielsweise dadurch erhalten werden, daß man in eine wäßrige oder wäßrig-alkoholische Lösung mit 0 bis 60 % Alkohol, 0,2 bis 10 Gew.% Blockpolymerisat nach der Erfindung einbringt.

Die kosmetischen Zubereitungen nach der Erfindung können weiterhin die üblichen kosmetischen Adjuvantien enthalten, wie Parfume, Farbstoffe, Konservierungsmittel, Weichmacher, Eindickmittel, anionische, kationische oder nicht-ionische Produkte, Silikone, um den Glanz zu verbessern und andere kosmetische Harze.

Die ausgezeichneten kosmetischen Eigenschaften der Zube-

reitungen der Erfindung sind der Gegenwart von wenigstens einer Sequenz der Formel I in den Polymerisaten mit zwei oder drei Sequenzen zu verdanken.

Tatsächlich ermöglichen Vergleichsversuche nachzuweisen, daß, wenn man die Sequenz der Formel I durch andere Sequenzen unterschiedlicher Struktur ersetzt, die dadurch erhaltenen Blockmischpolymerisate nicht in den Haarzubereitungen und insbesondere nicht in den Lacken oder Wasserwellenlotionen aufgrund der Tatsache verwendet werden können, daß bestimmte Eigenschaften mit diesen Arten der Zubereitung unverträglich sind.

Die Eigenschaften der Polymerisate mit zwei und drei Sequenzen nach der Erfindung weisen weiterhin eine ausgezeichnete Löslichkeit und Stabilität in Trägern, die in Lacken oder Wasserwellenlotionen verwendet werden, auf, sind nicht oder nur sehr schwach gegenüber Feuchtigkeit empfindlich, wodurch es möglich ist, zu vermeiden, daß das Haar schmierig und klebrig wird, und bilden einen geschmeidigen Film auf den Haaren, der angenehm zu berühren ist, wobei dieser Film leicht durch einfaches Bürsten oder Kämmen zu entfernen ist.

Die vorliegende Erfindung betrifft weiterhin ein Verfahren zur Fixierung der Haare, bzw. Frisur, das darin besteht, daß man eine ausreichende Menge einer Zubereitung nach der

Erfindung aufträgt, die Haare auf Wasserwellenrollen einrollt und durch Zuführung äußerer Wärme während etwa 3 bis 20 Minuten trocknet.

Nach einer besonderen Ausführungsform dieses Verfahrens verwendet man die Zubereitung sofort nach dem Spülen der Haare, die man vorausgehend shampooiniert hat.

Obwohl das Verfahren zur Herstellung von Blockpolymerisaten bekannt ist, hat die Anmelderin die Hauptetappen, die zu ihrer Bildung führen, dargestellt.

Diese Polymerisationen werden vorzugsweise durch Initiatoren, nämlich "Anionen" eingeleitet, die im allgemeinen Metalle der Gruppe I des Periodensystems der Elemente sind, wie Lithium, Natrium, Kalium, usw. oder die organischen Verbindungen dieser Metalle.

Als solche Verbindungen sind zu erwähnen Diphenylmethylnatrium, Fluorenyl-lithium, Fluorenyl-natrium, Naphthalinnatrium, Naphthalin-kalium, Naphthalin-lithium, Tetraphenyldiisodibutan, Phenylisopropylkalium.

Die Auswahl der Polymerisationsinitiatoren ist tatsächlich von großer Bedeutung, da sie die Struktur der Polymerisatsequenz bestimmen. So ermöglicht Naphthalin-natrium die Polymerisation so zu orientieren, daß man ein Mischpolymerisat mit "drei Sequenzen" erhält. Im Gegensatz dazu

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orientiert Phenylisopropylkalium oder Diphenylmethylnatrium die Polymerisation in der Weise, daß man Polymerisate mit "zwei Sequenzen" erhält.

Diese Polymerisationsreaktionen, die zur Bildung von Blockpolymerisaten führen, finden in aprotonischen Lösungsmitteln, wie beispielsweise Benzol, Tetrahydrofuran, Toluol, usw. statt.

Allgemein erhält man die Blockpolymerisate in der folgenden Weise. Zunächst stellt man eine Lösung des Initiators in dem ausgewählten Lösungsmittel her, gibt dann eines der Monomeren zu bevor man eine der beiden Sequenzen herstellt und gibt nach Polymerisation dieses Monomers das zweite Monomer zu, bevor man die andere Sequenz bildet. Am Ende der Polymerisation entaktiviert man das Blockpolymerisat mit einigen Tropfen eines Lösungsmittels, das Protonen enthält wie Methanol.

Wie oben ausgeführt, führt die Auswahl des Initiators zur Bildung eines Polymerisats mit zwei oder drei Sequenzen.

Allgemein bewirkt man die Reaktion, die zur Bildung von Blockpolymerisaten führt, bei einer Temperatur von etwa -70°C . Diese Polymerisationsreaktionen können im Hinblick auf die Herstellung von Blockpolymerisaten offensichtlich nicht mit Hilfe von Monomeren durchgeführt werden, die mo-

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bile Wasserstoffatome aufweisen, wobei solche Monomeren, beispielsweise Säuren, Amide, die am Stickstoff nicht substituiert sind, Alkohole, Verbindungen, die α -Carbonylwasserstoffe enthalten, sind.

Wenn man demzufolge Blockpolymerisate zu erhalten wünscht, die in einer ihrer Sequenzen Säurefunktionen usw. aufweisen, ist es nötig, Monomeren zu verwenden, die später mittels Reaktion zur Bildung dieser Funktionsart führen. Zu diesem Zweck kann man beispielsweise von Monomeren, die eine Esterfunktion aufweisen, ausgehen. Es ist dann durch Hydrolyse möglich, die entsprechenden Säuren zu erhalten.

Ein solches Verfahren kann verwendet werden, wenn man durch Methacrylsäurereste gebildete Sequenzen wünscht.

Um die Erfindung besser verständlich zu machen, folgen ausschließlich zur Erläuterung und ohne Einschränkung der Erfindung, mehrere Herstellungsbeispiele für Blockpolymerisate sowie mehrere Beispiele für kosmetische Zubereitungen, die diese Blockpolymerisate enthalten.

Beispiele für die Herstellung

Mischpolymerisate mit zwei Sequenzen

Beispiele 1 - 8

Beispiel 1 - Herstellung eines Polymerisats:

Lauryl-methacrylat-2-N,N-Dimethylamino-äthyl-
methacrylat

In einen Behälter mit einem Fassungsvermögen von 4 Liter, ausgestattet mit einem mechanischen Rührwerk, einer Bromampulle, einer Zuführungsröhre für Stickstoff, einer Eintauchröhre, die geeignet ist zu Entnahmen des Reaktionsgemischs und einem Thermometer, führt man 2 Liter wasserfreies destilliertes Tetrahydrofuran ein. Man kühlt dann den Behälter bei einer Temperatur von -60°C mit Hilfe eines Trockeneis-Methanolgemischs.

Die ganze Vorrichtung befindet sich unter einer Stickstoffatmosphäre, die sorgfältig durch Erhitzen auf 400°C in Gegenwart von Kupferfolien gereinigt wurde, wobei der Stickstoffstrom in gleicher Weise durch Leiten über wasserfreies Kaliumhydroxid oder über wasserfreies Magnesiumperchlorat gereinigt wurde.

Durch die Bromampulle gibt man tropfenweise unter Rühren 12,5 ml einer Lösung von Diphenylmethyl-natrium in Tetrahydrofuran (0,8 Mol pro Liter) unter weiterem Rühren 100 g reines Laurylmethacrylat im Verlauf von 15 Minuten zu.

Nach Rühren gibt man dann ebenfalls im Verlauf von 15 Minuten bei der gleichen Temperatur (-60°C) 100 g 2-N,N-Dimethyl-amino-äthyl-methacrylat zu.

Die Temperatur steigt langsam und nach dem die Wärmeabgabe der Polymerisation aufhört, deaktiviert man das Polymerisat

mit zwei Sequenzen, dessen beide Sequenzen durch das Laurylpolymethacrylat und das 2-N,N-Dimethylamino-äthylpolymethacrylat gebildet sind. Im allgemeinen führt man die zuletzt bezeichnete Stufe mit Hilfe von einigen Tropfen Methanol durch. Die Lösung wird dann praktisch farblos und man destilliert das Tetrahydrofuran ab und löst den Polymerisatrückstand in Chloroform und fällt dann mit Petroläther aus. Nach zwei Lösungen in Chloroform und zwei Ausfällungen in Petroläther trocknet man das Polymerisat unter reduziertem Druck.

Man erhält auf diese Weise ein Blockmischpolymerisat mit zwei Sequenzen mit einer Ausbeute von 80 %.

Die Elementaranalyse zeigt, daß das Polymerisat 45 Gew.% 2-Dimethylamino-äthylpolymethacrylat und 55 Gew.% Laurylpolymethacrylat gebildet ist.

Das Durchschnittsmolekulargewicht, errechnet in Toluol, beträgt 80.000.

Dieses Blockmischpolymerisat mit zwei Sequenzen ist in dem Freongemisch 11/12 (60/40) löslich; es ist ebenso löslich in absolutem Alkohol.

Dieses Blockmischpolymerisat mit zwei Sequenzen kann durch das Dimethylsulfat quarternisiert werden, und das auf diese Weise erhaltene Mischpolymerisat ist ebenso nützlich in Freon und absolutem Alkohol sowie in einem 50/50 Alkohol-

Wassergemisch.

Beispiele 2 - 8 (siehe Tabelle I)

Die Blockmischpolymerisate mit zwei Sequenzen in der Tabelle I sind nach dem gleichen Verfahren wie in Beispiel 1 beschrieben, hergestellt.

Mischpolymerisate mit drei Sequenzen

Beispiele 9 - 12 (siehe Tabelle II)

Diese Blockmischpolymerisate mit drei Sequenzen der Tabelle II sind nach dem gleichen Arbeitsverfahren wie in Beispiel 1 beschrieben, hergestellt.

Quarternisierte oder in die Salzform überführte Mischpolymerisate

Beispiel 13

In einen Behälter mit 500 ml Fassungsvermögen, führt man 200 g wasserfreies destilliertes Tetrahydrofuran und 40 g Blockmischpolymerisat nach Beispiel 2 ein. Nach vollständigem Lösen des Mischpolymerisats führt man 3,2 g destilliertes Dimethylsulfat ein und rührt die Lösung 24 Stunden bei Raumtemperatur. Man destilliert danach das Tetrahydrofuran unter reduziertem Druck.

Man erhält auf diese Weise mit 95%iger Ausbeute ein Blockmischpolymerisat aus 27,9 % Hexylmethacrylat, 55,6 % 2-N,N-Dimethylamino-äthyl-methacrylat und 16,5 % 2-N,N-Dimethylamino-äthyl-methacrylat, das mit Hilfe von Dimethylsulfat

quarternisiert ist.

Beispiele 14 - 21 (siehe Tabelle III)

Die in der Tabelle III angegebenen Polymerisate (Blockmischpolymerisate) sind nach dem gleichen Verfahren wie oben in Beispiele 13 beschrieben, hergestellt.

Beispiele 22 und 23 (siehe Tabelle III)

Diese in die Salzform überführten Polymerisate sind ebenso nach dem gleichen Verfahren wie in Beispiel 13 beschrieben, hergestellt.

In der nachfolgenden Tabelle I sind die folgenden Katalysatoren verwendet:

- a) Diphenylmethylnatrium
- b) Phenylisopropylkalium

Als Lösungsmittel zum Messen des Zahlenmittelwerts des Molekulargewichts wurden verwendet:

- c) Toluol
- d) Cyclohexanon

- x Die Einführung von Äthylenoxid erfolgt durch 4 Stunden langes Einperlen bei 60°C, wonach man das Mischpolymerisat mit Wasser reaktiviert.
- xx Nach Einführen von Octamethylcyclotetrasiloxan hält man die Temperatur 4 Stunden bei 60°C und entaktiviert dann das Polymerisat mit Wasser.

Tabelle I - Blockmischpolymerisate mit zwei Sequenzen

Bei- sp.	Monomer 1	Monomer 2	Menge (g) 1 2	Katalys.- lösung in THF (ml)	Katalys.- menge (mg)	Aus- beu- te %	Zahlenmit- telwert des Mole- kulargew.	Elementar- analyse C H N	Gew.-Verh von 1/2 in dem Mischpoly- merisat
2	Hexylmethacrylat	N,N-Dimethyl- aminoäthyl- methacrylat	135 130	60	2865(a)	75	36 000(c)	64,0 9,9 6,3	30/70
3	Butylmethacrylat	N,N-Dimethyl- aminoäthyl- methacrylat	132 130	60	2865(a)	85	24 000(c)	63,1 9,9 5,9	34/66
4	Methylmethacry- lat	N,N-Dimethyl- aminoäthyl- methacrylat	130 130	60	2865(a)	80	24 000(c)	60,8 9,0 4,1	54/46
5	Styrol	N,N-Dimethyl- aminoäthyl- methacrylat	100 50	60	474(b)	76	125 400(c)	82,6 8,4 2,7	69/31
6	Butylmethacry- lat	N,N-Dimethyl- aminoäthyl- methacrylat	250 150	40	3820(a)	78	31 600(d)	64,5 9,1 3,6	60/40
7 ^x	N,N-Dimethyl- aminoäthyl- methacrylat	Äthylenoxid	50 50	10	955(a)	55			89/11
8 ^{xx}	N,N-Dimethyl- aminoäthyl- methacrylat	Octamethyl- cyclo-tetra- siloxan	50 50	10	955(a)	63			277/23 5558928

Tabelle II - Blockmischpolymerisate mit drei Sequenzen

Bei- sp.	Monomer 1	Monomer 2	Menge (g) 1 2	Katalys.- lösung in THF (ml)	Katalys.- menge (mg)	Aus- beu- te (%)	Zahlenmit- telwert des Mole- kulargew.	Elementar- analyse C H N	Gew.-Ver- hältnis von 1/2 in dem Misch- polym.
9	Butylmethacry- lat	N,N-Dimethylamino-70 äthylmethacrylat	70	35	2640(e)	80	31 800(d)	65,9 8,8 4,8	46/54
10	Butylmethacry- lat	N,N-Dimethyl- aminoäthyl- methacrylat	250 150	200	8120(f)	75	22 000(d)	64,1 9,4 3,5	60/40
11	Styrol	N,N-Dimethyl- aminoäthyl- methacrylat	35 35	20	1510(e)	85	45 600(d)	76,9 8,9 4,1	54/46
12	N,N-Dimethyl- aminoäthyl- methacrylat	Butylmeth- acrylat	60 140	200	4060(f)	65	70 000(c)	64,2 9,2 3,8	43/57

Als Initiator verwendet: Lösungsmittel zum Messen des Molekulargewichts:

(e) Naphthalin-natrium
(f) 1,1-Diphenyläthylen-natrium
(c) Toluol
(d) Cyclohexanon

Die Blockmischpolymerisate 9 bis 11 sind solche des Typs: AAA-BBB-AAA

Das Polymerisat 12 hat die Sequenzfolge: BBB-AAA-BBB

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Tabelle III - Quarternisierte Polymerisate

Rei- spiel	Verwendetes Polymerisat von Beispiel Nr. Gewicht Nr. Gewicht (g)	Reagenz (g)	% der Quarter- nisierung oder Salzbildung	Aus- beute (%)	Zusammensetzung der erhaltenen Polymerisate in g/100 g		
14	3	40	3,2(a)	15,1	95	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, quarternisiert	31,5 51,9 16,6
15	4	40	3,2(a)	21,7	95	Methylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, quarternisiert	50,1 33,4 16,6
16	1	40	3,2(a)	19,2	90	Laurylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat quarternisiert	51,0 32,4 16,6
17	6	40	3,2(a)	25	95	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat quarternisiert	55,6 27,8 16,6
18	9	10	0,8(a)	18,5	95	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat quarternisiert	42,6 40,8 16,6
19	9	10	0,79(b)	18,5	90	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat quarternisiert	42,6 40,8 16,6

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Tabelle III - Quarternisierte Polymerisate (Fortsetzung)

Bei- spiel Nr.	Verwendetes Polymerisat von Beispiel Gewicht (g)	Reagenz (g)	% der Quarter- nisierung oder Salzbildung	Ausbeute (%)	Zusammensetzung der erhaltenen Polymerisate in g/100 g	
20	9	10	0,69(c)	18,5	90	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, quarternisiert
						43 41,2 15,8
21	10	40	0,8(a)	25	95	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, quarternisiert
						55,6 27,8 16,6
22	9	10	0,46(d)	37	96	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, in Salzform überführt
						44 32,5 23,5
23	9	10	1,14(e)	37	95	Butylmethacrylat 2-N,N-Dimethylamino-äthyl-methacrylat 2-N,N-Dimethylamino-äthyl-methacrylat, in Salzform überführt
						41,3 30,5 28,2

Mittel zum Quarternisieren oder zur Salzbildung:

- | | |
|--------------------------|----------------|
| (a) Dimethylsulfat | (d) Salzsäure |
| (b) β -Bromäthanol | (e) Milchsäure |
| (c) Äthylbromid | |

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Beispiele für ZubereitungenBeispiel A

Man stellt nach der Erfindung eine Wasserwellenlotion für Haare her, wozu man die folgenden Bestandteile mischt:

- Blockmischpolymerisat nach Beispiel 1, 2, 3, 7, 8, 13,
14, 16, 17, 19, 20, 21, 22 oder 23 2 g
- Äthylalkohol 50 g
- Wasser, q.s.p. 100 g

Nach Aufbringen dieser Lotion auf das Haar werden die Haare über Lockenwickel gerollt und dann unter einem Helm getrocknet. Man erhält auf diese Weise ausgezeichnete Wasserwellen, wobei die Haare geschmeidig und weich und angenehm zu berühren sind.

Beispiel B

Man stellt nach der Erfindung einen Haarlack durch Mischen der folgenden Bestandteile her:

- Blockmischpolymerisat, hergestellt nach Beispiel 1, 2, 3,
4, 5, 11, 12, 13, 14, 15, 16, 17, 18 oder 21 8 g
- Äthylalkohol, q.s.p. 100 g

25 g dieser Lösung konditioniert man in einer Aerosolflasche mit 45 g Trichlorfluormethan und 30 g Dichlordifluormethan.

Beispiel C

Man stellt nach der Erfindung einen Haarlack aus den fol-

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genden Bestandteilen her:

- Blockmischpolymerisat mit zwei Sequenzen, hergestellt nach Beispiel 1 2 g
- Trichlorfluormethan 45 g
- Dichlordifluormethan 40 g

Beispiel D

Man stellt nach der Erfindung eine Wasserwellenlotion für Haare durch Mischen der folgenden Bestandteile her:

- Blockmischpolymerisat mit zwei Sequenzen, hergestellt nach Beispiel 2, 3, 4, 13 oder 14 2 g
- Äthylalkohol 50 g
- Wasser, q.s.p. 100 g

Nach dem man die Haare schampoont hat, spült man sie und bringt die Lotion einheitlich auf. Danach werden die Haare über Lockenwickel eingerollt und getrocknet. Man erhält schöne Locken mit ausgezeichneter Haltbarkeit.

Beispiel E

Man stellt nach der Erfindung einen Haarlack durch Mischen der folgenden Bestandteile her:

- Blockmischpolymerisat mit zwei Sequenzen, hergestellt nach Beispiel 2, 3, 4, 13 oder 14 8 g
- Isopropylalkohol, q.s.p. 100 g

25 g dieser Lösung konditioniert man in einer Aerosolbombe

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mit 45 g Trichlorfluormethan und 30 g Dichlordifluormethan.

Beispiel F

Man stellt nach der Erfindung eine Wasservellenlotion für Haare durch Mischen der folgenden Bestandteile her:

- Blockmischpolymerisat mit zwei Sequenzen, hergestellt nach Beispiel 14 2 g
- Isopropylalkohol 50 g
- Wasser, q.s.p. 100 g

Beispiel G

Man stellt nach der Erfindung eine Wasserwellenlotion für Haare durch Mischen der folgenden Bestandteile her:

- Blockmischpolymerisat mit zwei Sequenzen, hergestellt nach Beispiel 16 2 g
- Äthylalkohol 50 g
- Parfum 0,1 g
- Wasser, q.s.p. 100 g

Sofort nach dem Spülen der Haare nach dem Schampooenieren, trägt man die Lotion auf das Haar auf. Die Haare rollt man dann über Lockenwickler und trocknet 15 Minuten. Die erhaltenen Wasserwellen haben eine ausgezeichnete Haltbarkeit, wobei die Haare glänzen und weich zu berühren sind.

Beispiel H

Man stellt einen Haarlack der folgenden Formel her:

- Blockmischpolymerisat mit zwei Sequenzen, herge-
stellt nach Beispiel 2, 3, 4, 13 oder 14 2 g
- Trichlorfluormethan 45 g
- Dichlordifluormethan 40 g

Beispiel I

Man stellt einen Haarlack in der folgenden Weise her:

Man verwendet ein Gemisch der folgenden Bestandteile:

- Blockmischpolymerisat mit zwei Sequenzen, herge-
stellt nach Beispiel 15 8 g
- Äthylalkohol, q.s.p. 100 g

Man führt 25 g der erhaltenen Lösung in einen Aerosolbe-
hälter mit 45 g Trichlorfluormethan und 30 g Dichlordi-
fluormethan.

Beispiel J

Man stellt einen Haarlack in der folgenden Weise her:

- Polymerisat nach Beispiel 1, 2, 3, 5, 11, 13, 16,
17 oder 21 2 g
- Trichlorfluormethan 59 g
- Dichlordifluormethan 39 g

Beispiel K

Man stellt einen Haarlack in der folgenden Weise her:

- Polymerisat nach Beispiel 5 oder 11 2 g
- Isopropylalkohol 23 g
- Trichlorfluormethan 45 g
- Dichlordifluormethan 30 g

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Beispiel L

Man stellt einen Haarlack in der folgenden Weise her:

- | | |
|--------------------------------|---------|
| - Polymerisat nach Beispiel 17 | 1,25 g |
| - Äthylalkohol | 48,75 g |
| - Kohlenmonoxid (5 Bar) | 2 g |

Beispiel M

Man stellt einen Haarlack in der folgenden Weise her:

- | | |
|--------------------------------|------|
| - Polymerisat nach Beispiel 21 | 1 g |
| - Äthylalkohol | 49 g |
| - Kohlendioxid (5 Bar) | 2 g |

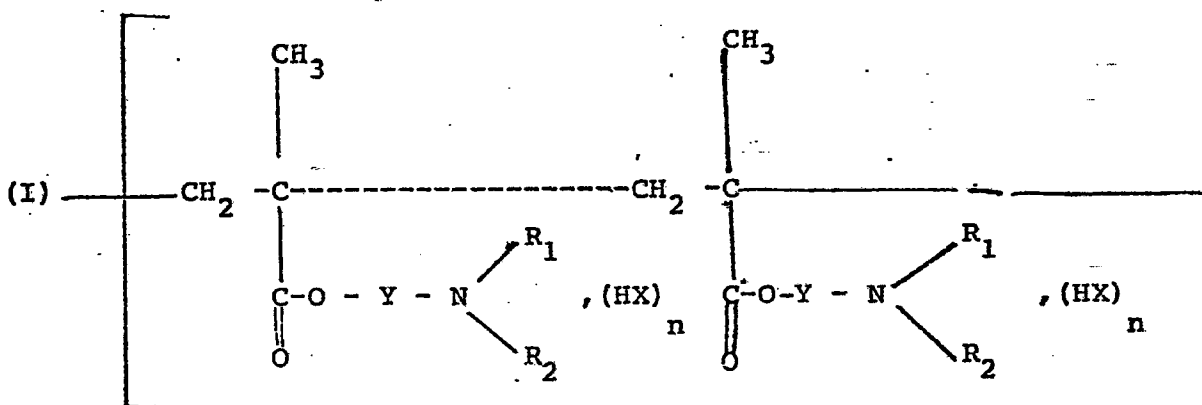
Beispiel N

Man stellt einen Haarlack in der folgenden Weise her:

- | | |
|--------------------------------|-------|
| - Polymerisat nach Beispiel 21 | 1 g |
| - Isopropylalkohol | 49 g |
| - Kohlendioxid (5 Bar) | 1,6 g |

Patentansprüche:

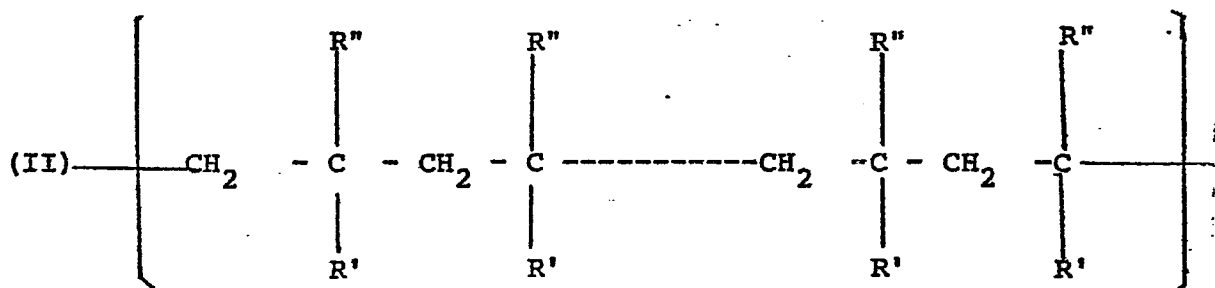
1. Zur Haarbehandlung geeignete kosmetische Zubereitungen, dadurch gekennzeichnet, daß sie in einem geeigneten kosmetischen Träger wenigstens ein Mischpolymerisat mit zwei oder drei Sequenzen aufweist, wobei es einerseits wenigstens eine Sequenz (A) der nachfolgenden allgemeinen Formel enthält:



- Y eine gesättigte Kohlenwasserstoffkette mit 2 bis 4 Kohlenstoffatomen oder eine Kohlenwasserstoffkette mit 2 bis 4 Kohlenstoffatomen, die durch Heteroatome, wie Schwefel oder Sauerstoff, unterbrochen ist, darstellt,
- die Reste R_1 und R_2 gleich oder verschieden sind, und Alkylreste mit 1 bis 4 Kohlenstoffatomen sind,
- $n = 0$ oder 1 ist, und HX eine organische oder Mineralsäure, nämlich Salzsäure, Bromwasserstoffsäure, Milchsäure und/oder Essigsäure ist, und

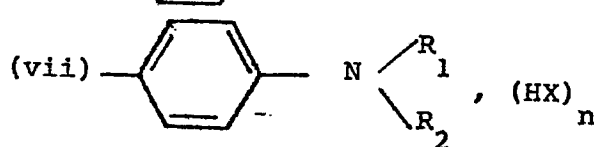
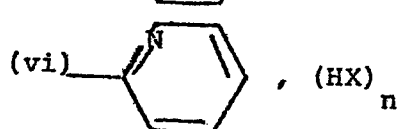
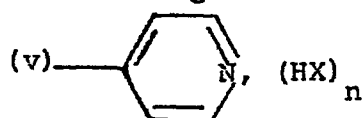
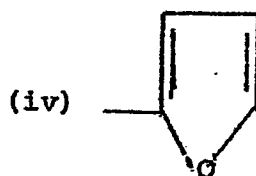
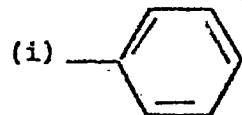
andererseits wenigstens eine Sequenz (B) enthält, die man durch Polymerisation eines auf anionischem Weg polymerisierbaren Monomers erhält.

2. Zubereitung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Sequenz B der nachfolgenden allgemeinen Formel entspricht:

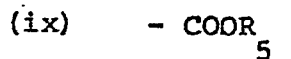
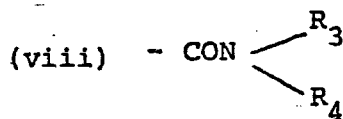


worin:

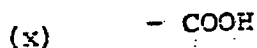
- R' eine Gruppe



R" ein Wasserstoffatom oder



und/oder

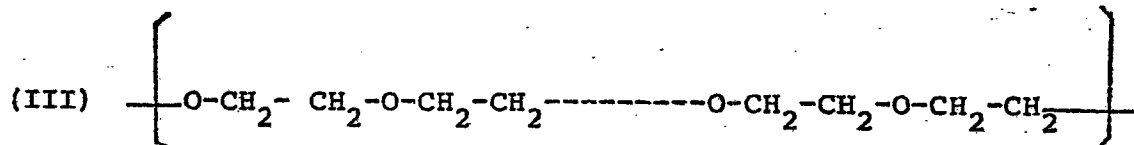


R" ein Methylrest

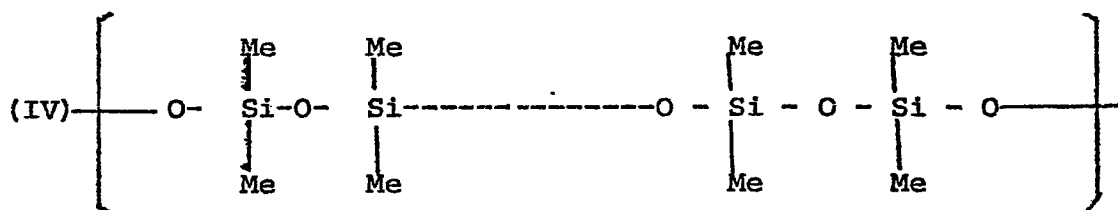
ist, und

worin die Reste R_1 , R_2 , n und HX die gleiche Bedeutung wie in dem Anspruch 1 haben, R_3 eine gesättigte Kohlenwasserstoffkette mit 6 bis 18 Kohlenstoffatomen, R_4 ein Methyl- oder Äthylrest und R_5 eine gesättigte Kohlenwasserstoffkette mit 1 bis 18 Kohlenstoffatomen ist.

3. Zubereitung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Sequenz B der nachfolgenden allgemeinen Formel entspricht:



4. Zubereitung gemäß Anspruch 1, dadurch gekennzeichnet, daß die Sequenz B der nachfolgenden allgemeinen Formel entspricht:



5. Zubereitung gemäß Anspruch 1, d a d u r c h g e -
k e n n z e i c h n e t , daß die Sequenz A der Formel I
hergestellt ist durch die Polymerisation eines Monomers,
wie Methacrylaten von 2-(N,N-Dimethylamino)-äthyl, 2-(N,N-
Diäthylamino)-äthyl, 2- $\sqrt{2}$ '-(N,N-Dimethylamino)-äthoxy-
äthyl und 2- $\sqrt{2}$ '-(N,N-Diäthylamino)-äthoxyäthyl.

6. Zubereitung gemäß einem der Ansprüche 1 und 5 , d a -
d u r c h g e k e n n z e i c h n e t , daß n = 0 ist
bei den Sequenzen A der Formel I, die tertiären Aminfunk-
tionen mit Hilfe eines Quarternisierungsmittels auf einem
Gehalt zwischen 0 und 100 % quarternisiert sind.

7. Zubereitung gemäß Anspruch 6, d a d u r c h g e -
k e n n z e i c h n e t , daß das Quarternisierungsmit-
tel Dimethylsulfat, Äthylbromid oder β -Bromäthanol ist.

8. Zubereitung gemäß einem der Ansprüche 1 und 2 , d a -
d u r c h g e k e n n z e i c h n e t , daß die Sequen-
zen B der Formel I erhalten sind durch Polymerisation eines
Monomers wie Styrol, 4-Methylstyrol, 2-Vinylpyridin, sein
Chlorhydrat und Lactat, 4-Vinylpyridin, sein Chlorhydrat

und Lactat, para-Dimethyl-aminostyrol, sein Chlorhydrat und Lactat, Methyl-, Äthyl-, Butyl-, Hexyl-, Octyl-, Lauryl- und Stearylmethacrylaten, Methacrylnitril, 2-Vinylfuran und N-Methyl-N-laurylmethacrylamid.

9. Zubereitung gemäß einem der Ansprüche 1 und 2, d a -
d u r c h g e k e n n z e i c h n e t , daß, wenn R'
in der Sequenz B der Formel II eine Carbonsäurefunktion
ist, diese Funktion mit Hilfe einer Mineral- oder organi-
schen Base neutralisiert, nämlich mit Ammoniak, Monoätha-
nolamin, Diäthanolamin, Triäthanolamin, Isopropanolaminen,
Morpholin, 2-Amino-2-methyl-1-propanol, 2-Amino-2-methyl-
1,3-propanediol oder auch in die Salzform in Form der Nä-
trium-, Kalium- oder Magnesiumsalze überführt ist.

10. Zubereitung gemäß einem der vorausgehenden Ansprüche,
d a d u r c h g e k e n n z e i c h n e t , daß das
Blockpolymerisat mit zwei oder drei Sequenzen ein Moleku-
largewicht zwischen 1000 und 1.000.000, vorzugsweise zw-
schen 2000 und 300.000 hat.

11. Zubereitung gemäß einem der vorausgehenden Ansprüche,
in Form von Aerosollacken, d a d u r c h g e k e n n -
z e i c h n e t , daß diese enthalten 0,2 bis 5 Gew.%
wenigstens ein Blockpolymerisat mit zwei oder drei Sequen-
zen, 0 bis 35 % und vorzugsweise 0 bis 25 Gew.% Alkohol
und 60 bis 99,8 Gew.% unter Druck verflüssigtes

Treibgas.

12. Zubereitung gemäß einem der Ansprüche 1 bis 10, in Form von Wasserwellenlotionen, d a d u r c h g e - k e n n z e i c h n e t , daß diese enthält in wäßriger oder wäßrig-alkoholischer Lösung mit einem Gehalt von 0 bis 60 % Alkohol, 0,2 bis 10 Gew.% wenigstens ein Blockpolymerisat mit zwei oder drei Sequenzen.

13. Zubereitung gemäß einem der vorausgehenden Ansprüche, d a d u r c h g e k e n n z e i c h n e t , daß sie weiterhin herkömmliche kosmetische Adjuvantien enthält, wie Parfume, Farbstoffe, Konservierungsmittel, Weichmacher, Eindickmittel, anionische, kationische oder nicht-ionische Produkte, Silikone oder andere kosmetische Harze.

14. Verfahren zum Fixieren der Haare bzw. der Frisur, d a d u r c h g e k e n n z e i c h n e t , daß man auf den Haaren eine ausreichende Menge einer Zubereitung gemäß einem der Ansprüche 1 bis 13 aufbringt, die Haare über Wasserwellenrollen einrollt, und sie unter Zuführung äußerer Wärme 3 bis 20 Minuten trocknet.

15. Verfahren gemäß Anspruch 13, d a d u r c h g e - k e n n z e i c h n e t , daß man die Zubereitung unmittelbar nach dem Spülen der Haare nach dem Shampoonieren aufträgt.